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**SPATIAL VARIATION AND BEHAVIOUR OF HEAVY
METALS (Pb AND Zn) IN THE URBAN SOILS OF
NORTH-CENTRAL NEWCASTLE, TYNESIDE**

CAROLINE FRANCES DILKS

**A thesis submitted in partial fulfilment
of the requirements of the
University of Northumbria at Newcastle
for the degree of Doctor of Philosophy**

October 2000

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ABSTRACT

This thesis focuses on the spatial variation, partitioning and behaviour of the heavy metals, Pb and Zn, within the soil of open public access areas in north-central Newcastle. The study examines metal concentration variation and the complexity of spatial variability, using geostatistical techniques to identify the level of spatial dependence and continuity between samples, collected at a variety of scales. It investigates the mobility and availability of Pb and Zn using sequential extraction to determine partitioning, examining top : sub soil enrichment ratios, in addition to using various statistical techniques to explore metal behaviour in relation to selected key soil properties. The study goes on to examine the severity of any contamination by comparison with published guidelines and trigger concentrations, and explores some of the wider legislative implications. Top soil total Pb and Zn concentrations were determined at four sites and three plots, in addition to metal fractionation, pH, organic content and CEC within the top and sub soil of plot I. Standard laboratory procedures were used where possible, with quality control checks employed to determine the reproducibility and efficiency of any non-standard methodologies.

The spatial distribution of contamination was characterised at all sampling scales by hot spot patterns of elevated concentrations, indicating that coarse scale sampling may be inadequate to reveal the degree of soil Pb and Zn variation. Spatial dependence / continuity of Pb and Zn concentrations was low, a dense sampling network being required ($0.5 \times 0.5\text{m}$) before clearly structured variograms could be produced. The two metals exhibited different partitioning characteristics; the reducible and oxidisable fractions being dominant for Pb, and the residual fraction for Zn. Pb was classed as being of higher potential hazard than Zn, displaying substantially higher concentrations. The soil properties did not consistently influence metal fractionation, although an increase in acidity increased both Pb and Zn mobility, whilst organic matter acted as an efficient scavenger for Pb, in addition to providing more exchange sites for the non-specific adsorption of Zn cations. CEC, associated with soil organic matter and clay content, was positively correlated with the oxidisable Pb fraction. The relative severity of Pb and Zn contamination varied according to the trigger thresholds used, although

under the UK ICRCL system only three samples collected from the four sites, and approximately 25% of samples from the three plots, were classed as contaminated with Pb. No equivalent threshold exists for Zn within open public access areas. The implications of these findings for the assessment and management of contaminated sites are discussed.

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ABBREVIATIONS

AAS	Atomic absorption spectrometry
ATSDR	Agency for Toxic Substance and Disease Registry
BCR	European Community Bureau of Reference
CEC	Cation exchange capacity
EA	Environment Agency
EDA	Exploratory data analysis
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Act
HPTULT	Highest probable threshold for uncontaminated land in Tyneside
ICRCL	Interdepartmental Committee on the Redevelopment of Contaminated Land
IQ	Intelligence Quotient
NRA	National Rivers Authority
PCA	Principal Components Analysis
ppm	parts per million
SEM	Standard error of the mean
SRS	Standard reference soil
SSSI	Site of special scientific interest
UK	United Kingdom
US	United States
USA	United States of America

CHEMICAL SYMBOLS

Al	Aluminium
Ca	Calcium
Cd	Cadmium
Cl	Chlorine
Co	Cobalt
CO ₃	Carbonate
Cu	Copper
Fe	Iron
Hg	Mercury
HNO ₃	Nitric acid
Mg	Magnesium
Mn	Manganese
NaNO ₃	Sodium nitrate
Ni	Nickel
Pb	Lead
Zn	Zinc

CHAPTER 1

INTRODUCTION

Summary

This chapter outlines the broad field of study, indicating gaps in the research and defining the main aims of the thesis. The chapter has been divided into 6 sections, which narrow to focus on the research problem. Section 1.1 briefly outlines recent research into soil heavy metal contamination within the urban environment, identifying potential human health risks. Section 1.2 defines the aims of the study, briefly describing how these aims have been met and outlining the main methodologies used. Section 1.3 provides a justification for the research and summarises the relative neglect of the area by previous researchers. Section 1.4 briefly outlines the content of each chapter, whilst the limitations of the study are described in section 1.5. Section 1.6 concludes the chapter, summarising the key achievements.

1.1 BACKGROUND TO RESEARCH

Concern stemming from the increased awareness regarding environmental hazards, such as heavy metal contamination, led to the introduction and revision of contaminated land legislation during the 1980s (Aspinall *et al.*, 1988; Thornton, 1991; Mellor and Bevan, 1999). In recent years, numerous studies have investigated elevated concentrations of heavy metals within the urban environment (Aspinall *et al.*, 1988; Culbard *et al.*, 1988; Douglas *et al.*, 1993; Kelly *et al.*, 1996; Mellor and Bevan, 1999), emphasis having shifted from mainly rural, agricultural land (Thornton, 1991). Studies have shown the urban environment to be affected by a wide variety of anthropogenic activities, including vehicular emissions and wear (Francek, 1992; Douglas *et al.*, 1993), past and present industrial activities (Aspinall *et al.*, 1988; Kelly *et al.*, 1996), metal smelting (Zachmann and Block, 1994; Rieuwerts and Fargo, 1995), and mining (Davies, 1978; Merrington and Alloway, 1994;) many of which have led to increased soil heavy metal concentrations (Culbard *et al.*, 1988). Concerns have been raised regarding city grown plants, particularly vegetables, which have been shown to accumulate metals via both root uptake and deposition of contaminants on above ground parts (Albasel and Cottenie, 1984; Hibben *et al.*, 1984).

In addition, recent studies have demonstrated the need to determine not only total heavy metal content within environmental samples, but also to identify the various physico-chemical forms of contaminant elements. These forms have been shown to have a profound influence on the availability, mobility and toxicity of metallic elements (Harrison, 1987; Ross, 1994) and hence potential hazard within the environment (Kofi Asante-Duah, 1996). Despite the numerous studies investigating the sources and assessing soil total heavy metal concentrations, knowledge of their fractionation remains limited (Alloway, 1995).

There exists a large body of evidence documenting the potential human health effects of heavy metals (Harrison and Laxen, 1981; Fergusson, 1990; Pirkle *et al.*, 1998; Mielke *et al.*, 1999), particularly Pb, which was ranked as the number one priority hazardous substance by the Agency for Toxic Substance and Disease Registry in 1992 (ATSDR, 1992). In severe cases, Pb poisoning has been associated with mental impairment, particularly in young children (BEES Environmental Health, 1997). Three principal pathways have been defined by which heavy metals enter the body; direct inhalation, ingestion of deposited dust (street, household and soil) and ingestion of foods and water contaminated with metals (Harrison and Laxen, 1981). Despite this for many years, the role of soil on human health has been neglected by the majority of soil scientists (Oliver, 1997).

1.2 RESEARCH AIMS

This investigation focuses on the spatial variation, partitioning and behaviour of the heavy metals, Pb and Zn, within the soil of open public access areas in north-central Newcastle. It attempts to determine the extent, severity and potential hazard of any contamination.

The investigation was conducted at four sites and three plots (Section 4.2.1) located within the geographical area classed as north-central Newcastle (Section 3.1), where variations in top soil heavy metal, Pb and Zn, concentrations were investigated on a variety of sampling scales, ranging from $100 \times 100\text{m}$ to $0.5 \times 0.5\text{m}$ (Sections 5.2.2 and

5.2.3). Sampling attempts to determine the degree of Pb and Zn concentration and spatial variation, identifying the level of complexity masked by coarse scale sampling. Geostatistical techniques, including the semi-variogram, have been used to assess the level of spatial dependence / continuity between metal concentrations at the plot sites (scales $25 \times 25\text{m}$, $5 \times 5\text{m}$, $0.5 \times 0.5\text{m}$), characterising the geographical variation at the three scales (Section 5.3). Kriging was used to produce a surface interpolation of Zn concentrations from the samples collected on the $0.5 \times 0.5\text{m}$ scale (Section 5.4).

Sequential extraction (Sections 2.5 and 4.3.1, Appendix 2) was used to determine the partitioning of the metals within the top and sub soil layers at the $25 \times 25\text{m}$ scale. Again, concentration and spatial variation have been investigated and patterns identified for the four fractions; exchangeable, reducible, oxidisable and residual, and total metals (Sections 6.2 and 6.3). Conclusions have been drawn regarding the partitioning and hence potential availability and mobility of top and sub soil Pb and Zn (Sections 6.2 and 6.3), in addition to levels of top soil enrichment (Section 6.5). Bivariate and multivariate statistical techniques have been used to assess relationships between the metal fractions and selected soil properties (pH, organic matter content and cation exchange capacity (CEC)) shown by previous research to affect metal retention mechanisms within the soil (Section 2.6). Levels and forms of any associations have been determined via correlation and regression, drawing inferences about the behaviour of the metals within the soil (Section 7.3).

The thesis aims are:

- To determine the complexity of soil heavy metal (Pb and Zn) variation masked by the coarse scale sampling of contaminated sites.
- To identify, using geostatistical techniques, the level of spatial dependence / continuity between samples collected on three different scales, $25 \times 25\text{m}$, $5 \times 5\text{m}$ and $0.5 \times 0.5\text{m}$, utilising the final variogram model to produce a surface interpolation of total metal concentrations.
- To examine, using a sequential extraction technique the partitioning and top soil enrichment of Pb and Zn, providing information regarding both concentration and spatial variation, in addition to relative mobility and availability.

- To investigate the behaviour, potential bioavailability and mobility of Pb and Zn within the soil by examination of the associations between total metals, metal fractions and a number of soil properties.
- To infer the sources of, and determine through the application of published legislative guidelines and trigger concentrations the relative severity of any pollution.

1.3 JUSTIFICATION FOR RESEARCH

Investigations conducted within the field of soil heavy metal contamination have highlighted a number of areas neglected by previous researchers, underlining the need for further, more detailed study. Thornton (1991) emphasised the relative lack of studies conducted within the urban environment, stressing that until relatively recently investigations have tended to focus on the rural environment, often with an agricultural emphasis. The author goes on to say, of urban areas, that more research is required to understand the dynamics and mobility of contaminants within their soils. Oliver (1997) noted the relative neglect of the effects of soil on human health by a large majority of soil scientists despite the view that soil is thought to be one of the main avenues for human exposure to Pb (Francek 1992).

The scarcity of detailed geographical studies assessing metal concentrations in the soils of British urban areas led Aspinall *et al.* (1988) to conduct an assessment of contamination in Tyneside soils. The study suggests several avenues for further investigation not least the examination of contaminated hot spots on Tyneside. The authors comment on the lack of detailed spatial studies of heavy metal concentrations within soil of the major industrial and urban areas of Great Britain and Europe, a surprise considering the well-documented adverse effects of such metals on human health. Aspinall *et al.* (1988) also highlighted the need for future work to ascertain the chemical forms of trace metals within soils, emphasising that the measurement of total and plant-available metal concentrations is not sufficient to forewarn of the possible health effects of potentially toxic metals in the environment.

Mellor and Bevan (1999) investigated top soil total and plant available Pb contamination within the Ouseburn catchment, Tyneside, going some way towards filling the research gaps highlighted by Aspinall *et al.* (1988). The study focuses on the spatial patterns, severity and mobility of Pb contamination within the catchment, and again highlights the need for more detailed research into the partitioning of Pb within the soil, and its relationship with other soil properties. The authors note the apparent lack of studies, conducted at an appropriately fine spatial scale, which focus on the spatial distribution of heavy metal contamination within urban areas, emphasising the effect of sampling density on the conclusions drawn from spatial sampling.

This present study examines the spatial patterns of Pb and Zn contamination within the urban environment of north-central Newcastle on a finer geographical scale than has previously been the case. Levels of spatial dependence are determined using geostatistical analysis, as a relatively new methodology within soil science (Oliver and Webster, 1991), with partitioning and hence availability and mobility of the metals determined using sequential extraction. The study infers the behaviour of Pb and Zn within the soil by examination of relationships between metal fractions and various soil properties. It goes on to assess, the hazard associated with the contamination by comparing metal concentrations with recognised legislative guidelines. The investigation aims therefore to fill several of the gaps highlighted in recent studies, particularly those of Aspinall *et al.* (1988) and Mellor and Bevan (1999).

1.4 THESIS OUTLINE

The main body of the thesis has been divided into 9 chapters, the content of which is outlined briefly below:

- Chapter 1 introduces the study, outlining the research problem and defining the main aims of the study. The chapter justifies the research, describing the limitations, in addition to briefly summarising the thesis.
- Chapter 2 reviews the literature and research issues relevant to this investigation. It develops a theoretical framework upon which the thesis is based, identifying issues

worthy of investigation. The chapter starts by looking at background literature then focuses on more specific areas of investigation.

- Chapter 3 defines and provides background information on the study area of north-central Newcastle. It then summarises, in addition to describing the four sites investigated during the study, the results of two key studies, conducted within the same geographical area; these were used to inform the sampling design adopted in this investigation.
- Chapter 4 outlines the methodology, theory and assumptions and justifies the choices made during the processes of sampling design and collection in the field, laboratory analysis and statistical analysis of data.
- Chapter 5 investigates the spatial patterns, variation and dependence of Pb and Zn focusing on increasingly fine sampling scales. The relative severity of any contamination is examined.
- Chapter 6 focuses on the spatial variation, partitioning and enrichment of Pb and Zn within the top and sub soil layers of plot I.
- Chapter 7 explores the relationships between the metals (Pb and Zn) and soil pH, organic matter content and CEC within the top and sub soil layers of plot I.
- Chapter 8 represents the main discussion chapter of the thesis. It attempts to pull together and explain the main findings of the three results chapters, placing these within the context of existing literature. It also intends to explore some of the implications of heavy metal contamination.
- Chapter 9 concludes the main body of the thesis. It reiterates the main findings of the investigation, and re-visits the original aims of the thesis. It goes on to consider the limitations of the investigation and to explore possible avenues for future research. The chapter also makes recommendations to managers investigating contaminated sites.

In addition the thesis includes 10 appendices.

- Appendix 1 outlines a number of systems of trigger thresholds and related guidelines for Pb and Zn in soils. These include the UK Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL) trigger concentrations, the Dutch ABC list and the 'New Dutch list'.
- Appendix 2 describes the sample collection and laboratory analysis conducted during the investigation, outlining the main techniques used.

- Appendix 3 describes and presents the results of the quality control programme established to assess the reproducibility and efficiency of two non-standard metal extraction techniques used for the investigation, namely microwave digestion and sequential extraction.
- Appendix 4 outlines the technical aspects and operation of Atomic Absorption Spectrometry (AAS) describing, in addition to the main components and calibration of the instrument, some of the more common problems and solutions associated with its use.
- Appendices 5 to 9 describe the theory and assumptions behind the statistics used throughout the thesis, including spatial dependence, surface interpolation, correlation and regression, principal components analysis and non-hierarchical classification.
- Appendix 10 contains tables of raw data.

1.5 LIMITATIONS

The author is aware of a number of limitations to the present investigation, not least the array of methodology existing for the extraction of heavy metals and determination of soil properties. Where possible well documented and tested techniques have been used to enable results to be compared to other relevant investigations. Quality control programmes have also been used to ensure high standards of reproducibility and efficiency. Sequential extraction techniques have been documented as being non-selective and allowing re-absorption of metals (e.g. Nirel and Morel, 1990; Tack and Verloo, 1995). Consequently, throughout the study metal fractions have been identified according to their operational or functional definitions, rather than their more specific geochemical classifications. Three key soil properties were selected to examine the availability and behaviour of the metals, although it is recognised that other soil properties might be of importance. Although geostatistical techniques have been used to provide valuable information regarding the spatial dependence of Pb and Zn, the author is again aware of limitations here. Insufficient samples are available for the reliable determination of anisotropy, despite the dense sampling scale producing clearly

structured omni-directional variograms (Webster and Oliver, 1990; Oliver and Webster, 1991).

1.6 CONCLUSION

This chapter has laid the foundations for the thesis, outlining the field of research, highlighting the research gaps and defining the main aims of the study. The research has been justified, the main methodologies listed and the thesis structure outlined. The limitations of the study have been recognised and justified, therefore allowing the thesis to proceed with a detailed description of the research.

CHAPTER 2

LITERATURE REVIEW

Summary

This chapter reviews the literature and research issues relevant to this investigation, developing a theoretical foundation upon which the thesis is based and identifying issues worthy of investigation. The chapter has been divided into 8 sections, which focus from general background to individual fields of study. Section 2.1 provides general information regarding definitions and sources of heavy metals as well as introducing the potential problems associated with their contamination and assessment. Implications for human health are outlined in section 2.2, and questions are raised as to the importance of soil as a pathway for heavy metal entry into the human body. Section 2.3 focuses on a number of studies which have assessed Pb and Zn contamination within the urban environment over the past 30 to 40 years, drawing some general conclusions before specific research areas are targeted in sections 2.4 and 2.5. Section 2.4 looks at spatial variation and the problems of interpretation of patterns, whilst section 2.5 reviews the technique of sequential extraction and its use in the assessment of the forms, behaviour and mobility of metals within the environment. Section 2.6 examines the effects of soil properties on heavy metal (Pb and Zn) retention within the soil system. Contaminated land legislation and policy are summarised in section 2.7, which also identifies the need for a new management approach. Section 2.8 concludes the chapter by reiterating the main gaps in the research, as identified by the review.

2.1 GENERAL

Davies (1980) defined heavy metals as those elements of the periodic table with a density of greater than 6gcm^{-3} , a vague classification which as stated by Alloway (1995) 'includes a very disparate group of elements'. However, the term 'heavy metals' is widely recognised, and used to describe all metals and metalloids associated with pollution and toxicity, including those essential at low concentrations for the sustenance of life. Heavy metals form part of the group known as trace elements, elements present in the soil at concentrations of only a few ppm. Recently, the term 'trace metal' has tended to replace that of 'heavy metal', but again the term is somewhat misleading, as a bulk soil sample which displays a low overall concentration of metal may have a high concentration at the micro-scale (Tiller, 1989), only identifiable by sub-sample analysis.

Heavy metals are natural components of the soil, present chiefly in forms which are unavailable to living organisms (Ross, 1994). Although toxic at high concentrations, some heavy metals are essential micro-nutrients; Zn, for example, acts as a catalytic or structural component in numerous enzymes of both plants and animals (Kieken, 1995). It is only when heavy metals are added to the soil in increasing quantities, i.e. higher than background levels, either from natural or anthropogenic sources, that they become a concern. Heavy metal pollution of the soil is acknowledged as a potential human health problem, as not only can metals enter the food chain indirectly through plant uptake, but they can also enter the body directly via the ingestion and inhalation of soil particulates (Harrison and Laxen, 1981). In addition, heavy metals may be leached from the soil into watercourses contaminating possible drinking water supplies.

Sources of heavy metals within the environment may be divided into two main groups: (a) natural or geological - those released by the weathering and erosion of geological materials, and (b) anthropogenic – those released as a consequence of human activities. Anthropogenic sources may be further sub-divided into primary and secondary; primary or agricultural as a consequence of working the land and secondary as a consequence of nearby activities (Figure 2.1).

Heavy metals are released into the environment in numerous forms, with single sources often emitting several forms of one metal. The form, along with ambient conditions, such as pH, temperature, redox potential, the amount of clay, organic matter and Fe and Mn oxides present, determine the fate of metals within the soil environment (Ross, 1994). Metals are held within the soil by a number of mechanisms, these include (1) non-specific adsorption of metal cations to the permanent charge sites of silicate clays and the pH dependent sites of organic matter, (2) specific adsorption of metal cations on oxide and hydroxide surfaces, (3) organic complexation whereby humic acids absorb metals by the formation of chelate complexes and (4) co-precipitation, occurring when a chemical reagent is simultaneously precipitated in conjunction with other elements (Section 2.6). The soil is a dynamic system hence changing edaphic conditions, for example, an increase in acidity or the degradation of organic matter, may result in the relocation of metals from one compartment to another. In addition animals such as earthworms can move soil over relatively large distances. The soil has a tendency to act as a sink for heavy metals, particularly Pb, which exhibits very low mobility once

incorporated into the soil system. Soil therefore has the potential to accumulate high concentrations of metals so, once polluted it is liable to remain so with the possibility of adverse consequences in the longer term.

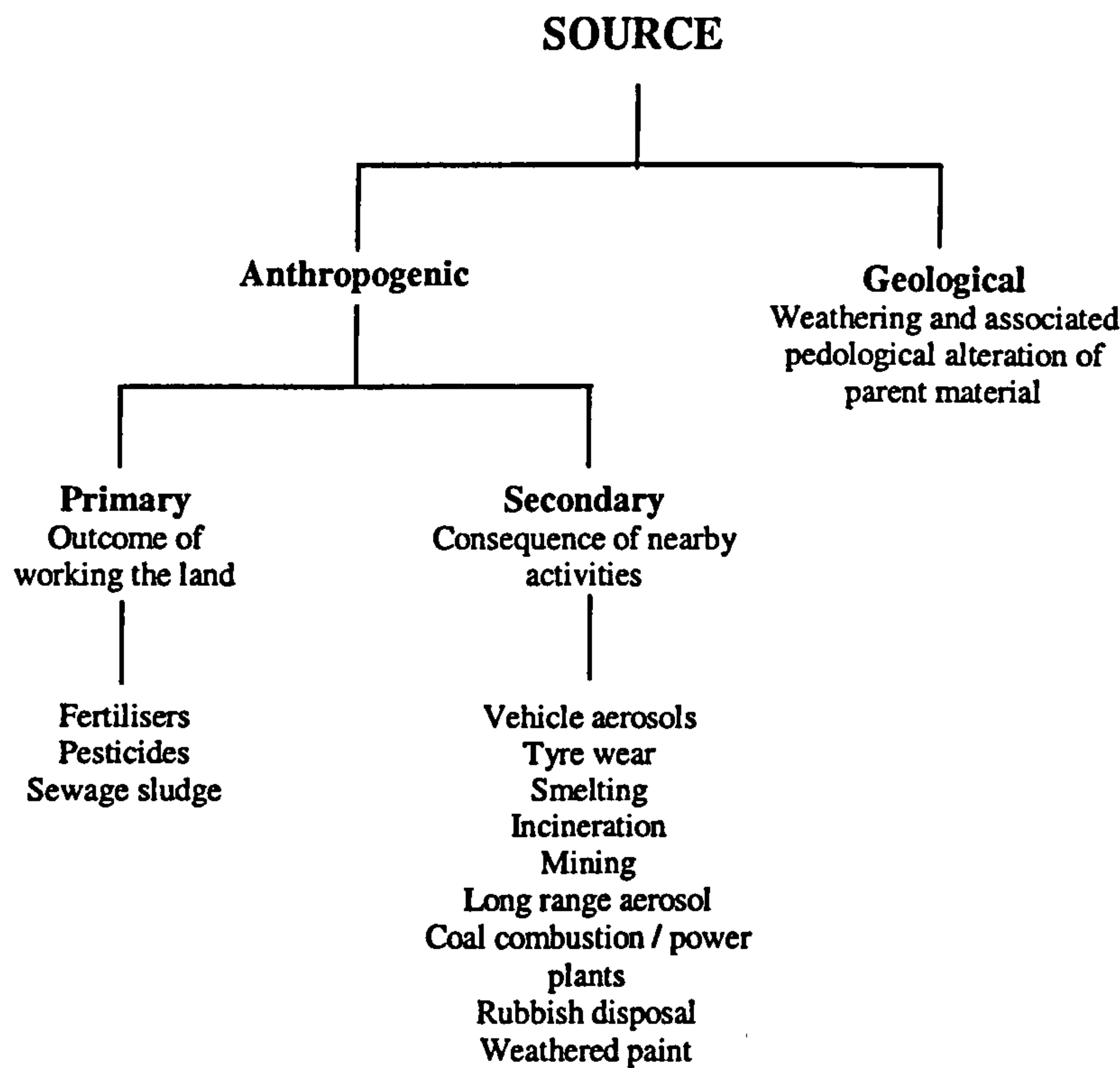


Figure 2.1 Sources of heavy metal contamination (Information from Ross, 1994)

2.2 HUMAN HEALTH IMPLICATIONS OF HEAVY METAL (Pb AND Zn) CONTAMINATION

Pb is toxic and exhibits no known function within the human body (Washington State Dept. 1996). It is an active and accumulative toxicant, the long-term exposure to which, even at low levels, can lead to irreversible damage to human health and possibly death. The human population has had a long history of exposure to Pb, which was in widespread use throughout many civilisations dating back as far as the Roman Empire. At that time Pb was used to line aqueducts, fabricate water pipes and for cooking utensils (Harrison and Laxen, 1981; Waternet, no date), it is likely therefore that both food and water were contaminated resulting in adverse health effects. Historically Pb

has also been used as a pigment in paint, an anti-knock agent in petrol and in some pesticides. Currently it is used in lead-acid batteries, fishing weights, lead shot and bullets as well as in the manufacture of some plastics (Washington State Dept., 1996). Today there are six major sources of exposure to Pb: leaded paint, leaded petrol, stationary sources such as mines, smelters and incinerators, dust and soil, food, and water. In 1992, the Agency for Toxic Substance and Disease Registry, ATSDR, ranked Pb as the number one priority hazardous substance (ATSDR, 1992).

Zn on the other hand is an essential element required by the body in low doses (ATSDR, 1989) to assist normal metabolism and the optimal functioning of more than 200 enzymes. Its compounds are found naturally within the air, soil and water, as well as being present in many foods, however despite a deficiency leading to poor health and a weakened immune system Zn may be harmful if too much is taken in. Zn is one of the most widely used metals in the world, being used in numerous alloys and for the protection of other metals through galvanising. Zn products are also used in a variety of consumer and health products, including dietary supplements, sun block, batteries and some poisons (Washington Dept. of Health, 1996). Zn is released into the atmosphere during the processes of mining, smelting, electroplating and metal manufacturing. Zn within urban discharges arises from waste-waters, fertilisers and the incineration of municipal wastes.

There are three principal pathways by which heavy metals enter the body (Harrison and Laxen, 1981); direct inhalation, ingestion of deposited dust (street dust, household dust and soil) and the ingestion of foods / water contaminated with metals. Once in the body, Pb will accumulate, with 95% being stored in the bones, teeth and soft tissue, regardless of the method of entry (ATSDR, 1990; Davydova, 1996; BEES Environmental Health, 1997). Young children are most at risk, as their bodies retain more inhaled Pb, some 40-50%, in comparison to adults 10-50% (ATSDR, 1992; Oliver, 1997). Children also absorb more ingested Pb, a particular problem in children displaying pica¹. Zn normally leaves the body in urine and faeces although it can accumulate within the human diet to the point of toxicity.

¹ pica - the swallowing of non-food items, such as soil.

The symptoms of Pb poisoning are non-specific, being similar to many other illnesses. The symptoms can include headaches, cramps, constipation, poor appetite, clumsiness, stomachache, vomiting, anorexia, sleeping problems, fatigue and lethargy. Pb affects four main systems within the body; the haematological system, the central nervous system, the renal system and the reproductive system (Hutton, 1987). Severe cases have been known to cause brain damage, mental retardation and reduced IQ, behavioural problems, anaemia, liver and kidney damage, hearing loss, hyperactivity and even death in young children (BEES Environmental Health, 1997). Once physical symptoms appear, the damage has already been done. Table 2.1 gives an indication of blood lead concentrations and the resultant problems caused in children.

Zn toxicity, the result of prolonged consumption of excess Zn, may interfere with the body's immune system and its ability to take in and use other essential minerals, such as Cu and Fe (ATSDR, 1989). The symptoms of toxicity include damage to the pancreas, irritability, muscular pain, loss of appetite, vomiting and anaemia (Washington Dept. of Health, 1996). The recommended safe intake of Zn is 15 µg/day, while levels in excess of 150 µg/day are toxic and will start to produce detectable changes and impairment of health (Oliver, 1997). The inhalation of Zn fumes produced when welding and soldering can cause 'metal fume fever', the long term effects of which are unknown.

level of poisoning	blood lead level (µg/dL)	effects / treatment
mild	15 – 19	effects subtle but will increase over time, lowers I.Q.
moderate	20 – 44	requires medical attention, chelation therapy may be used to remove Pb from body
high	45 – 69	full medical treatment is required, victim must be moved to a Pb free environment
emergency	> 70	medical emergency, brain damage may be seen in children

Table 2.1 Effect of blood lead concentration on children (adapted from BEES Environmental Health, 1997)

The effect of soil on human health has been disregarded by the large majority of soil scientists, although, it is now accepted that it may directly influence human health (Oliver, 1997). A review conducted by Mielke and Reagan (1998) confirmed that soil Pb could be associated with severe Pb poisoning, as concentrations were strongly related to blood Pb levels in both children and adults. The authors determined that abatement of soil Pb was effective at reducing blood Pb levels in young children. Health may be affected by direct ingestion and inhalation of soil particles, or the uptake or leaching of soil contaminants into food crops and ground water, respectively. The direct ingestion of soil has been shown to be an important pathway for Pb entering the human body in former smelting towns, despite appearing to be a less obvious source of exposure (Sheppard *et al.*, 1992).

A number of studies have been conducted to assess the effects of Pb in soil and dust particularly on children (e.g. Duggan, 1980; Jin *et al.*, 1997; Wong and Mak, 1997; Lanphear *et al.*, 1998; Pirkle *et al.*, 1998; Mielke *et al.*, 1999). Mielke *et al.* (1999) studied the contribution of soil Pb to blood Pb concentrations in children living within New Orleans, USA. Findings suggested a significant association between soil Pb and the blood Pb levels of children aged 6 and younger. Results of a survey conducted by Pirkle *et al.* (1998) investigating the blood Pb levels of >13000 people residing in the US, determined that 2.2% of the population displayed concentrations of >10µg/dl, the level of health concern for children. Jin *et al.* (1997) determined that children exposed to soil Pb levels of 1000ppm had blood Pb concentrations between 1.10 and 1.86 times higher than those exposed to soil Pb levels of 100ppm, and that children exposed to levels of 2000ppm displayed concentrations between 1.13 to 2.25 times higher. A significant reduction in blood Pb levels was seen as the result of the clean up of a residential area located on the contaminated site of an abandoned smelter in New Mexico (Eidson and Tollestrup, 1995).

Dubourg (1996) attempted to estimate the mortality cost of Pb emissions in England and Wales via the merging of epidemiological evidence, on dose-response factors, and economic valuation techniques. The author determined that, despite a significant decrease in Pb emissions over the last 20 years, in 1987 approximately 62 adult male

fatalities within urban areas could be attributed to airborne Pb, with an estimated economic cost of £92 million.

Soil heavy metals have also been found to have an adverse affect on plant growth (Albasel and Cottenie, 1984; Martin and Bullock, 1994), invertebrates, for example snails and woodlice, both of which show high accumulation of metals such as Pb, Zn, Cd and Cu when living in an ecosystem contaminated by heavy metals (Martin and Bullock, 1994) and bacterial communities (Roane and Kellogg, 1996; Zvyagintsev *et al.*, 1996). Roane and Kellogg (1996) saw Pb adversely affect the biomass, metabolic activity and diversity of bacterial communities, although resistant microbial communities did exist.

2.3 HEAVY METALS IN THE URBAN ENVIRONMENT: CONTAMINATED LAND

The 1960s saw the first investigations of heavy metal contamination within soils of urban areas. Purves and Mackenzie (1969), for example, compared heavy metal concentrations in soils of urban parks and permanent rural pastures in and around Edinburgh, Scotland, and found that the former displayed higher values. Prior to this studies tended to focus on the rural environment, often with an agricultural emphasis, as this land, used for the production of crops was considered to pose a more direct threat to human health. In the 1970s attention began to focus on the possible health implications of long term exposure to low levels of heavy metals, particularly Pb and Cd (Culbard *et al.*, 1988). Young children were identified as being most at risk from Pb contamination, more so than adults residing in the same area.

The complexity of the urban environment presents problems regarding the assessment of contaminated sites. Urban development and industrial activity within urban areas, in which the majority of the population live, determine that the soil may have been exposed to varying degrees of contamination. Continual overprinting and a combination of both natural and anthropogenic sources of these metals dictate that urban sites may have been exposed to several sources of contamination. In addition, historical land use records are often inaccurate or non-existent and hence past activities

difficult to ascertain, particularly as many sources of industrial pollution have been masked by changing land uses (Thornton, 1991).

Surface soil within inner city areas is frequently seen to contain considerable concentrations of Pb, much higher than that of rural areas (Douglas *et al.*, 1993). A study in Richmond, UK, found that top soils in developed areas of the London Borough displayed far higher concentrations of heavy metals than those in open green spaces (Kelly *et al.*, 1996). This study contradicted a Manchester based study which identified soil of inner city green spaces as containing the highest levels of EDTA extractable Pb (Douglas *et al.*, 1993). A study in residential Minnesota, identified localised areas of severe Pb contamination around private residences, the major source of which was Pb based exterior paint (Schmitt *et al.*, 1988). The authors determined that the contamination was more concentrated but less widespread than that produced as a result of many anthropogenic activities. Hewitt and Candy (1990) observed that soils in the urban environment of Cuenca, Ecuador contained elevated metal concentrations comparable to those observed in developed countries, noting that levels did not appear to be elevated outside the urban area. Urban soil pollution has been identified as exhibiting three dimensions, the spatial dimension related to distance from sources, the depth dimension concerned with soil stratification and a time dimension related to length of exposure to a given source (Douglas *et al.*, 1993).

Many urban heavy metal investigations have focused on the effects of vehicular emissions, now an historic source of soil Pb contamination within the UK and a number of other developed countries following the phasing out of leaded petrol, in addition to vehicular wear (Wheeler and Rolfe, 1979; Harrison *et al.*, 1981; Albasel and Cottenie, 1984; Tiller *et al.*, 1987; Ho and Tai, 1988; Francek, 1992; Douglas *et al.*, 1993; Fatoki, 1996; Fatoki, 1997; Singh *et al.*, 1997; Jaradat and Momani, 1999). Albasel and Cottenie (1984), for example, found pronounced Pb and Zn contamination along roadside verges and fields adjacent to roads and industrial zones in Belgium. Jaradat and Momani (1999) and Singh *et al.*, (1997) saw Pb burdens decrease with increasing distance from the road margins in Jordan and Lucknow, India, respectively. Fatoki (1997, 1996) identified similar patterns of soil Zn contamination in Alice, East Cape. Similarly, in Manchester, UK, Douglas *et al.* (1993) found the highest soil Pb concentrations directly adjacent to the roads, with concentrations decreasing rapidly

within the first few meters from the road and slowly thereafter; the decrease was identified as exponential. Jaradat and Momani (1999), Kelly *et al.* (1996) and Wheeler and Rolfe (1979) also noted an exponential decay in Pb concentrations with distance from roads. The majority of vehicular Pb was found to be deposited within 30 - 50m of roads, with background levels² being reached at approximately 50 - 60m. Tiller *et al.* (1987) investigated long distance transport, examining the dispersal of exhaust Pb from Adelaide, Australia into adjacent rural areas. They saw that 3% of the petrol derived Pb was dispersed beyond the immediate road zone, settling within 50km of the city centre. Pb tetraethyl remains a contemporary source of Pb contamination in many counties.

Other factors have been identified as contributing, to the pattern of heavy metal contamination within the vicinity of road networks, including, traffic density (Harrison *et al.*, 1981; Ho and Tai, 1988; Francek, 1992; Douglas *et al.*, 1993; Hamamci *et al.*, 1997) and the presence of and associated traffic congestion (Kelly *et al.*, 1996). Ho and Tai (1988) who studied concentrations of a number of heavy metals in roadside soils and grass in Hong Kong, found high levels of contamination within the highly urbanised northern part of the island where traffic density is highest. In their study, Harrison *et al.* (1981) determined that the highest concentrations of Pb and Zn were within soil samples taken from a highly congested roundabout. They attributed these levels to long term accumulation as a more heavily trafficked but newer motorway displayed lower concentrations. Prevailing wind direction and topography are also considered to play an important role (Francek, 1992; Hamamci *et al.*, 1997; Jaradat and Momani, 1999). Jaradat and Momani (1999) identified higher levels of soil metal contamination on the east side of roads in Jordan, in line with the prevailing wind direction, however Francek (1992) found no significant differences in Pb concentration between upwind and downwind sides of streets in Mt Pleasant, Michigan USA. The authors attributed this to inconsistent wind direction caused by the passage of weather fronts and eddying around trees and buildings.

In addition to roads, the geographical distribution of heavy metals within soils has been linked to past and present industrial activities, as illustrated by Kelly *et al.* (1996) in Wolverhampton, UK. Here elevated concentrations of Zn were found to be associated

² background levels – expected ‘natural’ concentrations of metals within soil of a certain area.

with Fe related industries, metalworkings, engineering and sewage works, whereas the lowest concentrations were found in the more rural outskirts of the city. Aspinall *et al.* (1988) also identified distinct geographical patterns of soil heavy metal (Pb, Zn, Cd) contamination which correlated well with past and present industry in Tyneside. Here, greatest contamination was found adjacent to the River Tyne and in parts of Gateshead where it was linked to the presence of incinerators and various modern industrial operations. In Falun, an urban area of central Sweden, high concentrations of soil Pb have been attributed to the disposal of wastes from mining and chemical industries (Lin *et al.*, 1998).

High levels of heavy metal contamination have also been associated with smelting (Burkitt *et al.*, 1972; Buchauer, 1973; Tiller and de Vries, 1977; Zachmann and Block, 1994; Rieuwerts and Fargo, 1995; Benin *et al.*, 1999; Fargo *et al.*, 1999), metal alloy production (Samanta *et al.*, 1995) and historic mining areas (Ward *et al.*, 1976; Davies, 1978; Merrington and Alloway, 1994; Merrington, 1995; Rieuwerts and Fargo, 1995; Shu and Bradshaw, 1995). Zachmann and Block (1994) found the soil and stream sediments in the vicinity of a Pb smelter near Clausthal-Zellerfeld, Germany to be highly contaminated due to airborne pollution and the dumping of waste slags. Fargo *et al.* (1999) confirmed the presence of high soil heavy metal concentrations in the proximity of a secondary smelter in Ladskrona, Sweden, determining that enrichment had occurred throughout the town, although distances >3.5km were not affected. On the other hand, Buchauer (1973) who investigated soil and vegetation contamination from two Zn smelters in Palmerton, determined that background concentrations of soil heavy metals were not reached until a distance of 16 to 39km from the smelter plants. The author found contamination distance to be dependent upon the metal and prevailing wind direction. Burkitt *et al.* (1972) also identified very high levels of Pb, Cd and Zn contamination near a smelting works in Avonmouth, Bristol, UK again with significant quantities being detected several kilometres away particularly in a downwind direction. At Te Aroha, New Zealand, near the Tui Mine soil heavy metal contents were also seen to decrease with distance from the treatment plant. Here, background levels were reached at a distance of >150m, contamination being a direct result of deposition of airborne dust from the plant. Davies (1978) sampled garden soils from numerous urban and rural areas throughout England and Wales. He found that older gardens displayed higher Pb concentrations than those of younger properties, suggesting that pollution

levels were increasing over time. He went on to suggest that such increases were a consequence of the fallout of coal ash from chimneys. However, higher concentrations could be the result of inheritance from a more polluted past.

Contaminated soil contributes to the composition of plants, raising concerns over the possible contamination of city-grown vegetables. Plants have the potential to accumulate metals via root uptake and by the deposition of contaminants on above ground parts. Hibben *et al.* (1984) state that vegetables grown in cities can be visibly injured and stunted by pollutants derived from vehicular exhausts and industrial discharges, a statement which was not substantiated by their investigation centred in Brooklyn, New York. This study compared Cd and Pb concentrations in seven leaf and five root and bulb crops grown in the city environment of Brooklyn and in a suburban environment, and found no significant differences. In a survey conducted in Greater Sydney, Australia, the authors discovered that in general, fruit contained the lowest and leafy vegetables the highest concentrations of Cd (Jinadasa *et al.*, 1997). Similarly, Voutsas *et al.* (1996) saw elevated levels of heavy metals, particularly Pb and Zn in leafy vegetables grown in Thessaloniki, Greece. Jones (1983) conducted a glasshouse pot experiment using soil collected from the vicinity of a galvanised steel tower in Toronto, Ontario, Canada. He found the highest Zn concentrations in lettuce grown in soil with the highest Zn contamination; concentrations in the tops and roots were found to be similar. Vegetables grown in the vicinity of a Pb – Zn smelter in Port Pirie, South Australia, have also been found to contain elevated metal concentrations (Tiller and de Vries, 1977). Albasel and Cottenie (1984) found heavy metal concentrations within plants growing in urban park lands to be significantly higher than in those growing in rural areas.

Plant uptake of metals varies as a function of soil conditions, notably pH and organic matter content (Ross, 1994), although concentrations in soils are not necessarily associated with high concentrations in plants. Soil conditions play an important role in determining the forms and fate of metals within the soil, and their availability for uptake. Techniques such as sequential extraction may be utilised in the determination of metal forms, and play a vital role in assessment of both the environmental impact and potential hazards associated with heavy metal contamination (Farmer *et al.*, 1983).

2.4 CONTAMINATED LAND: SPATIAL VARIATION

Over the past ten years a number of studies have focused on the spatial distribution of metal contaminants within soil, investigating variation and spatial dependence³ as well as developing models for surface interpolation. The scale of such investigations has varied dramatically, ranging from the examination of whole countries (Culbard *et al.*, 1988; Piotrowska *et al.*, 1994; White *et al.*, 1997) to 1ha plots (Boekhold and Van der Zee, 1992; Kuzel *et al.*, 1994). Many of these studies were characterised by large, short-range variation with occasional 'hot-spots' displaying values several orders of magnitude higher than the rest of the data set. These variations have caused problems with both the interpretation and presentation of data (Tiller, 1992).

A substantial degree of research has been conducted investigating the efficiency of various sampling patterns and sampling scales for the identification of contaminated hot spots. Three sampling patterns have been examined in detail, the regular grid, random and stratified random examples of which are given in Section 4.2.2. Fergusson (1992) developed a herringbone sampling design (Figure 4.4) the performance of which is thought to be optimal when little or no information is available regarding the spatial distribution of contaminants at a site. Much of this research has focused on the risks associated with failing to identify contaminated hotspots if they were to exist.

Culbard *et al.* (1988) examined Pb concentrations in soil and dust from 53 locations throughout Great Britain, in a survey commissioned by the UK Department of Environment. Sites were selected according to geographical location, industrial and urban development and to reflect differences in population; some mineralised areas were included as geochemical 'hot-spots'. Average soil Pb concentrations fell between 200 and 500µg/g for samples collected in most major cities, noticeable exceptions being Bristol and some of the London boroughs, which displayed higher average concentrations. Derbyshire villages, located in a former Pb mining area, displayed the highest level of Pb contamination, with an average concentration of 5610µg/g. Prohic *et al.* (1997) used similar techniques to determine geochemical patterns in soils of the

³ spatial dependence – the majority of soil properties vary continuously in space, with sites that are close together being more similar than those further apart; statistically sites therefore depend upon each other (Webster and Oliver, 1990).

Karst region of Croatia, following the collection of 420 samples on a 5×5 km grid scale. They related variation in soils to underlying geology, soil type, natural and anthropogenic influences.

In Poland, Piotrowska *et al.* (1994) found that soils in the south and west of the country contained significantly higher and more variable concentrations of Pb than those in the north east, eastern and central regions. Results were represented on a three dimensional spatial plot and the highest concentrations found to be associated with point sources of contamination, including smelters and power plants. Southern Poland also experiences atmospheric inputs of Pb from adjacent regions of Germany and former Czechoslovakia.

A number of authors have conducted investigations at the city scale (Aspinall *et al.*, 1988; Douglas *et al.*, 1993; Kelly *et al.*, 1996; Markus and McBratney, 1996; Pitchel *et al.*, 1997). Pitchel *et al.* (1997), measured heavy metal concentrations in the surface soil along parallel transects across Warsaw, Poland, comparing their 1996 data with that collected in 1976. Pb contamination had extended up to and sometimes beyond the city limits, although levels had declined in certain areas. The highest concentrations were found in samples collected near the city centre and in the vicinity of heavy metal industries. Levels of Zn had, on the other hand, remained relatively constant. Markus and McBratney (1996) who sampled using a stratified random technique within 1 ha square areas, identified a degree of spatial clustering of topsoil Pb, Zn and, Cd concentrations in Glebe, Australia. In general they found little variation between samples, but the range of concentrations were wide, Pb for example displaying values of 20 - >20000 mg/kg. They also found that in some cases adjacent samples contained very different concentrations, thus highlighting the problems of interpretation of spatial variation in an urban environment.

Douglas *et al.* (1993) and Aspinall *et al.* (1988) both conducted investigations within the UK, looking at Manchester and Tyneside, respectively. Douglas *et al.* (1993) associated high concentrations of Pb with roads, historical industry and housing, commenting that grassed areas in the city were liable to carry legacies from earlier urban land uses. Aspinall *et al.* (1988) identified a strong local variability of soil metal

concentrations despite the comparatively coarse intra-urban scale of the investigation ($1 \times 1\text{km}$ grid). These authors concluded their study by stressing the need to examine the contaminated 'hot-spots' of Tyneside in greater detail. This was undertaken using a finer geographical scale of sampling ($200 \times 200\text{m}$ grid) by Mellor and Bevan (1999) who focused on the spatial distribution of Pb in the top soils of public access areas in the Ouseburn catchment, Tyneside. Mellor and Bevan (1999) identified a 'hot spot' pattern to the spatial distribution, determining that the highest soil Pb concentrations were within the central and southern parts of the catchment; areas associated with a legacy of past industry and urban development.

In recent years, the emphasis of spatial investigations into soil contamination has started to change with geostatistical techniques, originally developed to evaluate ore deposits within the mining industry, being employed to assess the spatial dependence of contamination. Kriging, primarily a prediction technique, is being utilised to enable surface interpolation from point samples (Webster and Oliver, 1990), hence estimating continuous surfaces. A number of kriging techniques exist, although ordinary kriging is thought to be the most suitable for the estimation of pollutant concentrations within the soil (Oliver and Webster, 1991) (Appendix 6). Within risk assessment investigations however, disjunctive and indicator kriging are also valuable tools. Disjunctive kriging enables determination of the probability that data does or does not exceed a given threshold, of particular importance in areas where estimates of pollutant concentrations are close to a threshold. Indicator kriging however, utilises separate variograms produced for a series of cutoff (indicator) values to determine the proportion of an area above or below a threshold. For example, when examining soil Pb contamination, a threshold of 2000mg/kg maybe set and the actual concentrations replaced by 0 or 1 depending on whether they exceed the threshold value. A variogram is then determined for the indicator threshold and the method of ordinary kriging used to produce predictors and interpolate the surface.

These techniques have been utilised in both large (Tao, 1995; Markus and McBratney, 1996; Frangi and Richard, 1997) and small-scale investigations (Boekhold and Van der Zee, 1992; Kuzel *et al.* 1994; Arrouays *et al.* 1996). Tao (1995) utilised the techniques to map topsoil Cu, Pb and Hg concentrations in the Shenzhen area of China. The author

was able to reveal the geographical variation of the metals by the production of variograms ⁴ (Appendix 5), based on the 83 point samples analysed. The variograms were utilised as models for kriging. The largest inconsistencies between measured and calculated values were found where the element contents in the soil varied dramatically. Frangi and Richard (1997) and Markus and McBratney (1996) conducted similar analyses in northern France and Glebe, Australia, respectively. Frangi and Richard (1997) interpolated a 100km² area from 125 point samples collected systematically in concentric circles; pollutant distribution was closely related to the dominant wind direction. The authors concluded that the spatial representation of Pb and Cd concentrations showed the extent of the pollution and enabled the level and extent of contamination to be delimited. Markus and McBratney (1996) who sampled on a 100 × 100m grid concluded that map surfaces could have been more accurate had the sampling intensity been greater.

Arrouays *et al.* (1996) investigated short-range variability of trace elements in soil at a contaminated site that had been used for the production of lead tetraethyl since 1938. Four samples were collected from each of 15 sample point locations, using a sampling pattern adapted from the French National Soil Quality Monitoring Network. Variograms were produced, one for lags⁵ 0.36m to 0.70m and a second for lags 10m, 20m and 30m. Local variability was the same within 1m as for the whole plot, leading to the conclusion that the nugget effect⁶ was mainly due to micro heterogeneity. Kuzel *et al.* (1994) investigated Cd variation on two scales, 100 × 100m and 10 × 10m, at an agricultural field located within the Czech Republic. They used directional variograms to demonstrate spatial heterogeneity or anisotropy at the 10 × 10m scale, i.e. that Cd varied differently in different directions, a phenomenon demonstrated by the non-coincidence of directional variograms. Sampling at the 100 × 100m failed to identify the true nature of contamination at the site.

Many of the above investigations have highlighted problems regarding the spatial interpretation of soil heavy metal contamination. Some have shown elements to be

⁴ variogram – graph representing the average variance of pairs of samples located certain distances (lags) apart.

⁵ lag – average distance between pairs of samples.

⁶ nugget effect – when the variance of a sample compared with itself, i.e. lag = 0, does not equal zero.

randomly distributed, even at short range ($<1\text{m}$) (Arrouays *et al.*, 1996), whereas others have identified spatial dependence between samples. Interpolation has also been seen to be inaccurate in areas where soil element concentrations have varied dramatically (Tao, 1995). Many of the problems associated with interpretation and modelling can be related to large micro-scale variations, i.e. hot spots, in urban soil heavy metal concentrations.

2.5 SEQUENTIAL EXTRACTION

Recent years have seen recognition of the need to determine not only total heavy metal content within environmental samples but to identify the physico-chemical forms of contaminant elements. Forms have been seen to profoundly influence the availability, mobility and toxicity of metallic elements and hence their potential hazard within the environment (Harrison, 1987). The chemical form of Pb, for example, appreciably affects the level of gastro-intestinal absorption when ingested into the human body. Form has also been seen to affect the availability of metals for plant uptake (Ross, 1994). Methods such as sequential extraction are now being utilised in an attempt to understand the behaviour of various forms of such elements (Farmer *et al.* 1983; Davidson *et al.* 1994; Tack and Verloo, 1995) and therefore enable a more accurate assessment of potential hazard.

Sequential extraction procedures consist of subjecting a given sample to a series of increasingly strong reagents under specified conditions in the laboratory, thus isolating metals according to their ease of extractability (Nirel and Morel, 1990). The techniques use reagents which simulate both natural and dramatic changes that can occur within the environment, such as changes in pH or redox status (Rauret, 1998). The changes occur at an accelerated pace, however, compared to those within the natural environment.

Tessier *et al.* (1979) developed the first widely used procedure, enabling the partitioning of particulate metals into five fractions: exchangeable, bound to carbonates, bound to Fe and Mn oxides, bound to organic matter and residual. A variety of sequential extraction techniques have since been developed utilising different sets of reagents to separate metals within both soils and sediments into four to eight fractions (Tessier *et al.*, 1979;

Gibson and Farmer, 1986; Kim and Fergusson, 1991; Ure, 1991; Yong and Galvez-Cloutier, 1993; Davidson *et al.*, 1994; Real *et al.*, 1994; Li *et al.*, 1995).

Exchangeable phase metals, are those considered to be non-specifically adsorbed and subject to ion exchange, i.e. they can be replaced by non-competing cations. Metals precipitated or co-precipitated as natural carbonates are classified as being the carbonate phase and may be released by the application of an acid. Those attached to amorphous or poorly crystallised Fe, Al and Mn oxides, are known as the hydroxide-oxide phase and may be released by the application of a reducing agent. The organic phase represents metals held by the mechanisms of complexation, adsorption and chelation, and released as a result of organic matter degradation. Metal fractions only extractable by digestion with strong acids at elevated temperature are classed as residual; these are normally held within the lattice of silicate minerals (Yong and Galvez-Cloutier, 1993).

Davidson *et al.* (1994) evaluated the BCR technique, a three-stage extraction procedure, designed by the European Community Bureau of Reference. The technique, which separates metals into exchangeable, reducible and oxidisable forms, was seen to be sufficiently repeatable and reproducible. The authors extracted three sets of three samples at weekly intervals and found that even for elements far from their detection limits, significant within-set and between-set variation occurred. The between-set variation was generally seen to be greater than within-set variation and the method was deemed to be reproducible enough to obtain useful information regarding heavy metal fractionation.

Narwal *et al.* (1999) investigated the associations between heavy metals and soil components in naturally metal rich soils of Norway using a seven-step sequential extraction technique. They determined that Cd was the most easily desorbed, and hence most mobile and bioavailable. Zn was found to be strongly associated with the fractions less available to plants. Gibson and Farmer (1986) conducted a study in Glasgow, Scotland utilising a six step extraction procedure to determine the partitioning, availability and mobility of Pb, Zn, Cd, and Cu within 90 top soil samples, collected from gardens, open spaces, parks and agricultural land. Measures of total concentration allowed an order of metal contamination to be determined, which for Glasgow was Pb > Zn > Cu > Cd. Sequential extraction determined an order of mobility, calculated on the

basis of percentage metallic partitioning between the 'exchangeable' and 'carbonate bound' phases. The order of mobility was found to be $\text{Cd} \gg \text{Pb} > \text{Zn} > \text{Cu}$; on average, 13% of Pb and 10% of Zn were found within these phases. The order of overall environmental hazard was classed as $\text{Pb} > \text{Cd} > \text{Cu} > \text{Zn}$. Pb and Zn were also seen to have a strong association with the final three fractions, the hydroxide-oxide, organic and residual phases and hence severe resistance to downward mobility. In their study, Maskall and Thornton (1998) determined that only a small proportion of soil total Pb and Zn were in a readily mobile form. A high proportion of Pb was associated with the carbonate and specifically adsorbed phase. These results were mirrored by a study conducted in the Czech Republic (Szakova *et al.* 1999). Using the BCR sequential extraction technique these authors determined that Cd was more mobile than Zn; 18% and 55% of total Cd and Zn were found to be in residual form.

Although useful, sequential extraction procedures are not without problems. These include the non-selectivity of reagents, i.e. the attacking of components other than those specified, and the possibility of re-adsorption of metals (Nirel and Morel, 1990; Tack and Verloo, 1995). Doubt has therefore been cast on the usefulness of these procedures within the field of geochemistry, although they are considered useful within the field of environmental chemistry, where they are used for a different purpose (Real *et al.*, 1994). The techniques provide the environmental researcher with information regarding the forms in which heavy metals are held within soil, sediment and water systems, the potential availability of metals for uptake and the extent of their mobility, including the conditions which would cause them to be mobilised.

The identified metal fractions have been defined in a number of ways. They have been defined functionally, for example 'plant available fractions', operationally, according to the reagents or processes used in their extraction, or as particular compounds or states of the element (Davidson *et al.*, 1994). Concern over selectivity has seen a move away from the more specific geochemical classifications outlined above towards operational or functional definitions (Whalley and Grant, 1994; Ure, 1996). These definitions embrace a number of chemical entities that share a common function but the precise function of which is indeterminate.

2.6 EFFECTS OF SOIL PROPERTIES ON METAL MOBILITY AND AVAILABILITY

Within the soil system, the fate of toxic metals is dependent upon a number of factors, these being edaphic conditions, for example pH and organic matter content, the initial chemical form of the metal and the plants and animals within the system (Ross, 1994). However, knowledge of the chemistry and speciation remains limited despite the vast array of work investigating the sources and assessing soil total Pb concentrations.

Heavy metals are retained within the soil system by 6 main compartments, the soil solution, adsorption to the surface of clay and organic matter, precipitated forms, Fe and Mn Oxides, alkaline earth carbonates and silicate lattices (Alloway, 1995). Metal cations are retained by the permanent negative charge sites of silicate clays and the pH dependent sites of organic matter by non specific electrostatic adsorption, the strength of the attraction depending on the charge or valency and metal ion hydration (Ross, 1994). Metal ions compete for the exchange sites with more abundant cations such as Ca^{2+} and Mg^{2+} hence strong attraction is rare. Higher valency ions display a greater replacing power as do ions with a low degree of hydration (Alloway, 1995). The mechanisms of specific adsorption, whereby heavy metal cations are exchanged with surface ligands to form bonds with lattice ions, better explain the retention of cations within the soil as they result in ions being adsorbed to a far greater extent. These complexes most readily occur on oxide and hydroxide surfaces (Ross, 1994; Evans, 1989). Again the mechanism is strongly pH dependent and dependent on the hydrolysis of the metal ion. Co-precipitation and organic complexation, also provide mechanisms for metal retention in soils. Co-precipitation occurs when a chemical agent is simultaneously precipitated in conjunction with other elements and can occur at any rate, and by a number of mechanisms. Organic complexation on the other hand is the processes by which humic acids adsorb metals by forming chelate complexes (Alloway, 1995). Soil properties such as pH, organic matter content, CEC, clay content and presence of Fe and Mn oxides therefore exert influences on the stability of heavy metal ions within the soil system.

Numerous studies have investigated the effects of soil properties on heavy metal retention and solubility within the soil system of both polluted and non-polluted soils

(McKenzie 1980; King, 1988; Sanchez-Camazano *et al.*, 1998; Hooda and Alloway, 1998). pH and CEC have been identified as the main soil properties involved in the immobilisation of heavy metals, although soil organic matter also plays an important role. In general, pH exerts the greatest influence on metal solubility, with solubility and hence availability increasing with decreasing pH (Chuan *et al.*, 1996; Rieuwerts *et al.*, 1998). Conflicting evidence has been published regarding the effects of organic matter, although in general, higher organic matter contents are thought to lead to higher metal retention (Sauve *et al.*, 1997; Hooda and Alloway, 1998). Hargitai (1995) suggested that the type of organic matter may be more important than the amount.

Rieuwerts *et al.* (1998) used secondary data and empirical models to investigate the influence of soil properties on the solubility of metals, predicting the proportion of bioavailable (extractable) metals from total concentrations. Analysis showed that pH had the greatest single effect on the proportion of extractable metals. Similarly, Chuan *et al.* (1996) determined that pH greatly affected heavy metal solubility in soil, with solubility dramatically increasing in soils of pH <3.5. Solubilities were seen to increase as redox potential decreased, more acidic, reducing conditions being the most favourable for metal solubility. pH exhibited a greater effect than redox potential. Hooda and Alloway (1998) determined that pH, CEC, organic matter content, clay content and CaCO₃ were all correlated with soil metal retention. Similarly, Sanchez-Camazano *et al.* (1998) found significant correlations between total metal concentrations and organic matter content in soils collected from uncultivated, unpolluted soils of Valladolid, Spain. Associations between soil Pb and clay were also noted. Sauve *et al.* (1997) on the other hand, saw no significant associations between Pb and organic matter.

A study conducted by King (1988) determined that soil Zn retention was most strongly affected by pH, whereas Pb retention was more strongly affected by clay content and Fe oxides. King also identified a general although weak relationship between metal retention and exchangeable cations. McKenzie (1980) when studying the adsorption of heavy metals on Mn and Fe oxides found that the adsorption of Pb by Mn oxides was up to 40 times greater than that by Fe oxides. The author also noted that Pb was more strongly adsorbed than Cu, Co, Mn, Ni or Zn. An increase in soil pH, from 3.0 to 5.0

and 5.0 to 6.5 for Pb and Zn, respectively, was seen to increase adsorption on Fe oxides from nearly zero to almost 100%.

A number of laboratory simulation studies have drawn similar conclusions regarding the effects of soil properties on heavy metal retention within soils. Harter (1983) for example, studied Pb, Cu, Ni and Zn adsorption and desorption in pH adjusted soils, confirming that the amount of metal retained was dependent upon pH. Retention was found to increase dramatically for pHs above 7.0 to 7.5. The author also noted that soils exhibiting the highest CEC were found to exhibit higher sorption of the metals, although this relationship could not be quantified. Organic matter content was similarly thought to be a major factor in metal retention, explaining differences between top and sub soil levels, but again no correlation was found between metal retention and this property. Lumsdon *et al.* (1995) also investigated the influence of a number of soil properties on metal retention within a laboratory using pH adjusted soils. They determined that the proportion of metal adsorbed increased within increasing pH with the amount retained dependent upon the organic matter content of the soil. Soil containing a higher organic matter content was found to adsorb a greater amount of metal at a given pH. Chloride ions exerted virtually no effect on the retention of Zn, the effect of Cl⁻ ions on soil metal retention being directly related to the ability of the metal to form complexes with the ions.

2.7 LEGISLATION AND POLICY

Concerns regarding contaminated land began to increase during the 1960s (Tadesse *et al.*, 1994). However, it is only in recent years, with an upsurge of more serious damage caused by old landfills and abandoned contaminated sites, that contaminated land has been considered a serious problem (Richards *et al.*, 1996). Contamination processes themselves are not new, often going back many decades having left an unwanted legacy. Concern stemmed from the increased awareness of both government bodies and the general public regarding potential hazards, such as heavy metal contamination, and led to the introduction of new legislation and revision of existing legislation in many developed countries (Aspinall *et al.*, 1988; Thornton, 1991; Richards *et al.*, 1996). Remediation strategies evolved rapidly, and the complexity of the potential problem,

coupled with the need for immediate guidance, led to the development and adoption of a variety of remediation approaches (Sheppard *et al.*, 1992). The legislation aims to protect the soil environment from further contamination.

Britain developed a system of '*fitness for use*', where land would be restored to a condition suitable for its planned use. This is a system that has traditionally tended to be purely reactive, i.e. only being enforced when land is to be developed (Griffiths and Board, 1992). The driving forces behind this approach were the use of the land and the effects upon local amenities. Historically, land has been controlled through planning law, with pollution only being assessed when land was to be sold. The approach was that of 'buyer beware'⁷, but with the introduction of the Environmental Protection Act 1990 (EPA, 1990), the emphasis shifted towards 'polluter pays'⁸, particularly in light of the production of The Register for Potentially Contaminated Land, a register set up to collate information on contaminated sites.

EPA (1995) defines contaminated land as:

'any land which appears to the local authority in whose area it is situated to be in such a condition, by reason of substances in, on or under the land that- (a) significant harm is being caused or there is a significant possibility of such harm being caused; or (b) pollution of controlled waters is being, or is likely to be caused'

The Act determines that such land is the responsibility of local authorities and lays out, in conjunction with the paper produced by the Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL, 1987), guidelines regarding the registration and treatment of such areas within the UK. The legislation defines a series of tentative, land use dependent, 'trigger concentrations'⁹ which relate to total metals; as yet 'action values'¹⁰ have not been specified (Appendix 1). These guidelines are used to assist decision makers in selecting the most appropriate use for a site and in deciding

⁷ 'buyer beware' – remediation of contaminated land is the responsibility of the owner of that land; therefore if you buy land that its contaminated you are responsible for its clean up.

⁸ 'polluter pays' – the polluter of land, if found, is responsible for its remediation.

⁹ trigger concentrations – series of specified guidelines for contaminants in soil. Levels of contamination above these guidelines require investigation.

¹⁰ action values – specified levels of contamination above which remediation / clean up must be conducted.

whether remedial action is required (Dellow, 1994). The guidelines are not retrospective and therefore do not apply to sites that have already been developed. The Act attempts to move environmental protection towards an holistic approach via the recognition of the fact that the environment operates as an integrated system (Richards *et al.*, 1996). Overall responsibility for environmental protection in the UK now lies with the Environment Agency formed in 1996 as a result of the 1995 EPA. In contrast to the UK, the Netherlands and the USA have adopted what has become known as the 'multifunctionality' approach, remediating all land to a set standard, suitable for any use (Griffiths and Board, 1992; Contaminated Land, 1996). The Dutch approach has had an enormous impact worldwide (Tiller, 1992).

The Dutch were the first nation in Europe to enforce legislation regarding remediation of contaminated land following a pollution incident in residential Lekkerkerk, near Rotterdam (Griffiths and Board, 1992). The response to this incident was a national inventory of possible polluted sites which, in 1985, included more than 6000 sites, leaving the country particularly concerned about public health. A nationwide cleanup operation ensued and hence the need to develop an extensive legal framework. The Netherlands is one of the most heavily polluted countries in Europe, susceptible due to its geographical location, from both national and across boarder contamination. The lowland nature of the country, approximately one quarter of which is below sea level, determines that the water table is close to the surface of the soil. Many soils are marshy or water logged and hence reducing in nature determining that, metal contaminants may be more readily available. The high density of population within the Netherlands determines that land is intensively used with landuse frequently changing hence soil contamination can cause a serious problem.

In 1983 the Dutch Soil Clean Up Act led to the issue of what became known as the 'ABC list', a three tier system of legislative guidelines, specifying (A) background levels, (B) levels at which the site must be further investigated and (C) clean up concentrations (Appendix 1). The Dutch C, or clean up values in addition to being more stringent than the UK ICRCL guidelines cover a wider number of contaminants. These guidelines have since been modified and renamed the 'New Dutch List', a

comprehensive list of potential contaminants proposing both optimum¹¹ and action concentrations for pollutants in soil and groundwater (Appendix 1). The revision of the Dutch guidelines was based on the background levels of contaminants in rural soils and the general 'risk' to both human health and the environment (Sheppard *et al.*, 1992).

The USA has defined guidelines both at the federal and state level, the result of which has been the introduction of a wide range of quality standards across the individual states (Griffiths and Board, 1992). As with the Dutch guidelines, the USA has developed limits that are more stringent than the UK. Soil quality guidelines must be both practical and scientifically defensible, although despite this many have tended to be set on the basis of professional judgement, for example the UK ICRL trigger guidelines and the Dutch ABC list, rather than scientific research. This may lead to questions regarding their validity and economic defensibility (Sheppard *et al.*, 1992).

The majority of current published guidelines, regarding heavy metal contaminants, quote values relating to total metal concentrations. As stated by Gupta *et al.* (1996) 'these values are excellent criteria to define the extent of metal build up of contamination in soil.....but for the prediction of ecological impact total content is of little value', as metal concentrations within plants have been insufficiently correlated with soil total metal content. These authors propose a new risk assessment and management concept involving a three level evaluation system. The system defines guideline values, trigger values and clean-up values, whilst also incorporating three metal fractions and hence providing a clear scheme to assess potential exposure. The authors suggest developing guidelines for total, mobile and mobilisable metals and that guidelines would be exceeded if any one or more of the fractions exceeded specified levels. The mobile fraction provides a good indication of the potential vertical movement of contaminants and hence their implications for groundwater pollution, whilst the mobilisable fraction provides information regarding potential hazard if soil conditions were to change (Flavin and Harris, 1991; Gupta *et al.*, 1996). A similar, but not so comprehensive scheme has been in place in the German State of Baden-Württemberg since 1993, and Switzerland since 1996. Here guidelines based on total

¹¹ optimum concentrations – maximum concentration at which soil is deemed uncontaminated, values correspond with the 'background' level expected within a particular soil.

and mobile / bioavailable metals within soil have been accepted. Current legislation is such that worldwide there is a myriad of remediation guidelines, many of which are based on the Dutch ABC list. Ultimately it is essential that there is a move towards the development of a universal and comprehensive system.

2.8 SUMMARY

Since the 1960s research has identified potential contamination problems associated with soil in the urban environment, with heavy metal contamination linked to historical and contemporary industry, mining, waste disposal and vehicular emissions. Gupta *et al.* (1996) likened the soil to a 'chemical time bomb' which must be diffused before it explodes emphasising that although a polluted soil may not cause immediate toxic effect, the potential for danger should conditions change is very real. In 1992, ASTDR ranked Pb as the number one priority hazardous substance.

Young children have been classed as the most at risk from Pb contamination, with soil thought to be one of the main avenues for human lead exposure (Francek, 1992). Studies have shown children to retain more Pb within their bodies than adults, bioavailability being associated with metallic form. The mobility and availability of Pb and Zn within the soil have been linked to the soil binding mechanisms and various soil properties, in particular, pH, organic matter content and CEC. Over the past 20 years, sequential extraction techniques have been developed to determine the fractionation of metals within the soil, although they have sometimes been criticised for lack of selectivity. Despite this, such techniques are well used, valuable tools for the determination of heavy metal partitioning.

Over the past ten years, a number of studies have focused on the spatial distribution of heavy metals within soil, examining spatial variability at a variety of sampling scales. Many studies have identified hot spot patterns of contamination that make determination of the extent of contamination difficult. Recent years have seen the use of geostatistical techniques within soil science and land survey, enabling determination of spatial continuity and production of surface interpolations to a high degree of

reliability. Such techniques are useful for determining the hazard associated with contamination.

During the 1980s many European countries independently developed contaminated land legislation, hence, there exists a wide range of guideline and 'trigger' concentrations for heavy metal contaminants within soil. In addition, a number of remediation strategies exist, including the Dutch multifunctionality and the British fitness for use approaches. As yet, the majority of guidelines specify total metal concentrations only, despite metallic forms being known to affect mobility, availability and potential hazard. Ultimately it is essential that there is a move towards the development of a universal and comprehensive legislative system.

CHAPTER 3

STUDY AREA

Summary

This chapter defines and provides background information regarding the area classed by the investigation as north-central Newcastle. The chapter has been divided into three sections, which provide general information about the area and summarise the results of two previous studies conducted within the same geographical area. Section 3.1 includes information regarding the physical location, topography and geology of north-central Newcastle, in addition to both historical and contemporary land use. Section 3.2 describes investigations conducted by Aspinall et al. (1988) and Mellor and Bevan (1999), both of which looked at heavy metal contamination within the top soil of public access areas in Tyneside. The study conducted by Mellor and Bevan (1999) was used as a precursor to this investigation. Section 3.3 describes the four sites examined during this present investigation providing background information including physiography, vegetation cover landuse.

3.1 NORTH-CENTRAL NEWCASTLE

The area classed by the investigation as north-central Newcastle encompasses a substantial proportion of Newcastle-upon-Tyne adjacent to the city centre. The area, approximately 80km², defined using the 1991 ward boundaries for Newcastle includes the 12 most northerly wards, covering approximately the same geographical area as the Ouseburn catchment as defined by Mellor and Bevan (1999) (Section 3.2.2). The area stretches from beyond Dinnington in the north to the outskirts of Heaton, Jesmond and Fenham in the south and from High Heaton and Gosforth to the east, to Callerton in the west (Figure 3.1). The region exhibits a definite north east / south west urban / rural divide.

North-central Newcastle is an area of generally low relief, although a narrow, incised section of steeper relief runs from South Gosforth between Jesmond and Heaton to Byker following the course of the lower Ouseburn River (Figure 3.1). The solid geology consists of Carboniferous Middle Coal Measures, including a mixture of resistant sandstones, softer shale marine bands and coal deposits. This is covered by a layer of glacial till with a deposit of fluvial-glacial sands and gravels in the centre of the region (Mellor and Bevan, 1999). The region is transversed by a major structural

feature, the 90 fathom fault, which runs WSW-ENE through the centre of the study area. The dominant soil types are gleys and brown earths of the Brickfield and Hallsworth Series, the texture of which varies according to parent materials (Mellor and Bevan, 1999; Jarvis *et al.*, 1984).

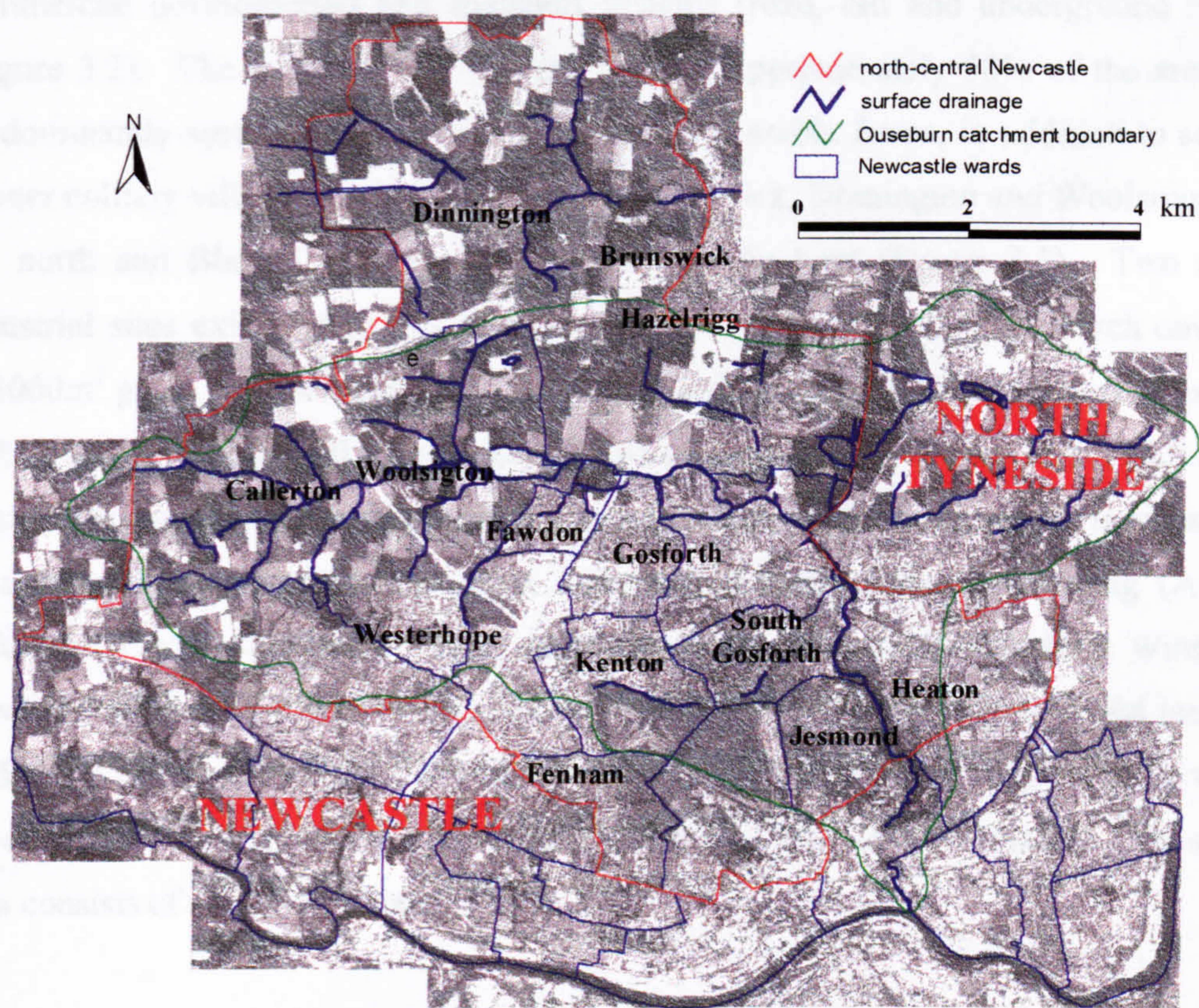


Figure 3.1 Area classed as north-central Newcastle.

The majority of north-central Newcastle is drained by the river Ouseburn, which rises in the west at Callerton pond (NZ 1764 6849), and flows for approximately 14km before joining the River Tyne at Byker (NZ 2627 6456). From its source, the river follows an easterly route through agricultural land before entering the urban reaches. The river’s course takes it through several residential areas before turning southwards at Gosforth to flow through two major amenity areas for the city, Jesmond Dene and Jesmond Vale. The north of the region is drained by the Hartley Burn, a small tributary that rises just west of Newcastle International Airport (NZ 2160 7230). The Burn flows east through agricultural land, and the nature reserve and lake north of Bruswick before joining the

Seaton Burn (NZ 2398 7350) within the geographical area of North Tyneside (Figure 3.1).

North-central Newcastle encompasses a wide variety of land uses, including residential developments, agricultural land, recreational and amenity areas, industrial and commercial developments and transport systems (road, rail and underground metro) (Figure 3.2). The northern and western regions, approximately 50% of the area, are predominantly agricultural supporting a number of arable farms, in addition to several former colliery villages, including Hazelrigg, Bruswick, Dinnington and Woolsington to the north and Black Callerton and Callerton to the west (Figure 3.1). Two major industrial sites exist within this area, Newcastle International Airport which covers a 341000m² green field site near Woolsington, approximately 10km north west of the city (NZ 2000 7170) (Turnbull 1994) and Brunswick industrial estate (NZ 2270 7250) to the west of Brunswick village (Figure 3.2). Approximately 2.5% of the region is given over to industrial development, the main industrial activities being packaging (Airport Industrial Estate, Kingston Park), pharmaceutical production (Sterling Winthrop, Fawdon), food processing (Greggs, Gosforth and Nestlé, Fawdon) and mixed industry (industrial estate, Bruswick). The remainder of the region consists of quite dense urban development, the major land use being residential (34%). Approximately 15% of the area consists of recreational land (Figure 3.2).

The majority of north-central Newcastle is of fairly low conservation value, although the whole of the rural area encompassed by the Ouseburn watershed (Figure 3.1) is set aside as 'green belt' (NRA, 1993). A 37ha site at Gosforth lake, within Gosforth Park (280ha), has been designated as an SSSI and is managed as a nature reserve by the Natural History Society of Northumbria. Two main areas of woodland exist within the region, one at Woolsington and the second at Gosforth lake. Jesmond Dene (45ha), one of the most extensively used parklands in the area, follows the deeply incised lower stretch of the Ouseburn. A number of other important areas of public amenity land are located within the region, including the Town Moor (140ha), Nuns Moor (120ha), Leazes Park (30ha), and Hazelrigg (40ha) and Brunswick (35ha) nature reserves (Figure 3.2). The Town and Nuns Moors, two areas of old common land, located towards the south of the region are used for grazing of cattle during the summer months. The Town Moor is also the location of the annual 'Hoppings' funfair held in late June (Section

3.3.1). In addition there are five golf courses within the region, located at Fawdon, Gosforth, North Gosforth, Nuns Moor and Westerhope (Figures 3.1 and 3.2).

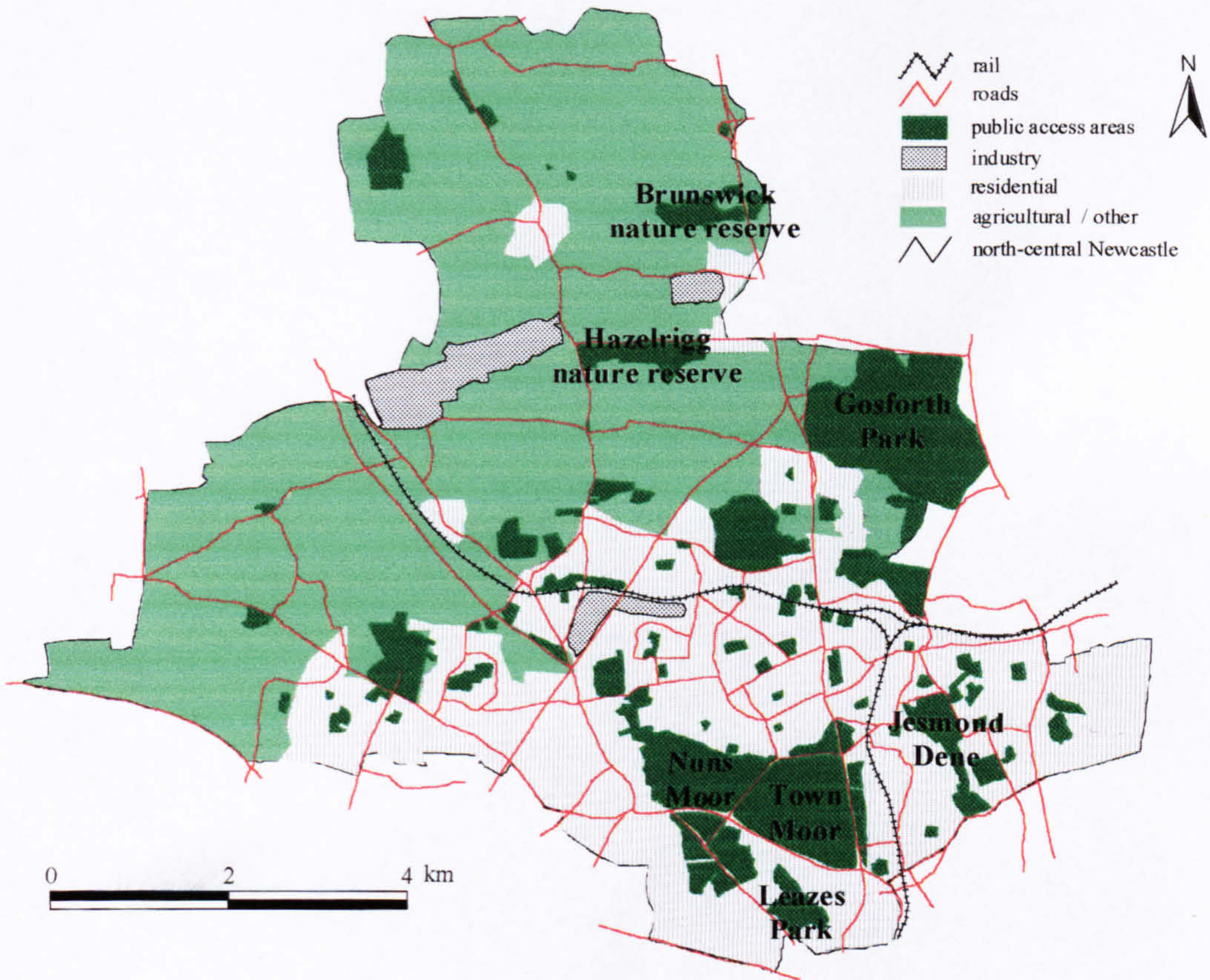


Figure 3.2 Contemporary land use in north-central Newcastle.

Historically north-central Newcastle has been subject to widespread coal mining, in the form of both deep pits and surface workings, most notably at South Gosforth (Turnbull, 1994). The 13th and 14th centuries saw the first opening up of coal seams in and around Newcastle (British Association for the Advancement of Science, 1949), with one of the regions earliest recorded pits opening at Kenton in 1683 (Palmer, 1993; Welford, no date). The 18th century saw pits at Dinnington, Brenkley and Prestwick in the north in addition to the more central areas of Coxlodge, Fawdon and High Heaton (Watson, 1996; Walker, 1994; Heaton Local History Group, 1990). Further pits were excavated during the 19th century including Jesmond colliery, Spital Tongues colliery and the

Jubilee and Regeant pits of Gosforth (Taylor, 1993; Airey, 1989). Significant pits were also located at Callerton and Westerhope in the west of the region (Turnbull, 1994). The most recent workings have been at an open cast site at Mill Hill Farm, west of Dinnington and a drift mine between Dinnington and Hazelrigg, both of which had closed by 1994 (Watson, 1996). In addition, an area close to Woolsington was used for open cast coal extraction between 1991 and 1994 (Turnbull, 1994) (Figure 3.3).

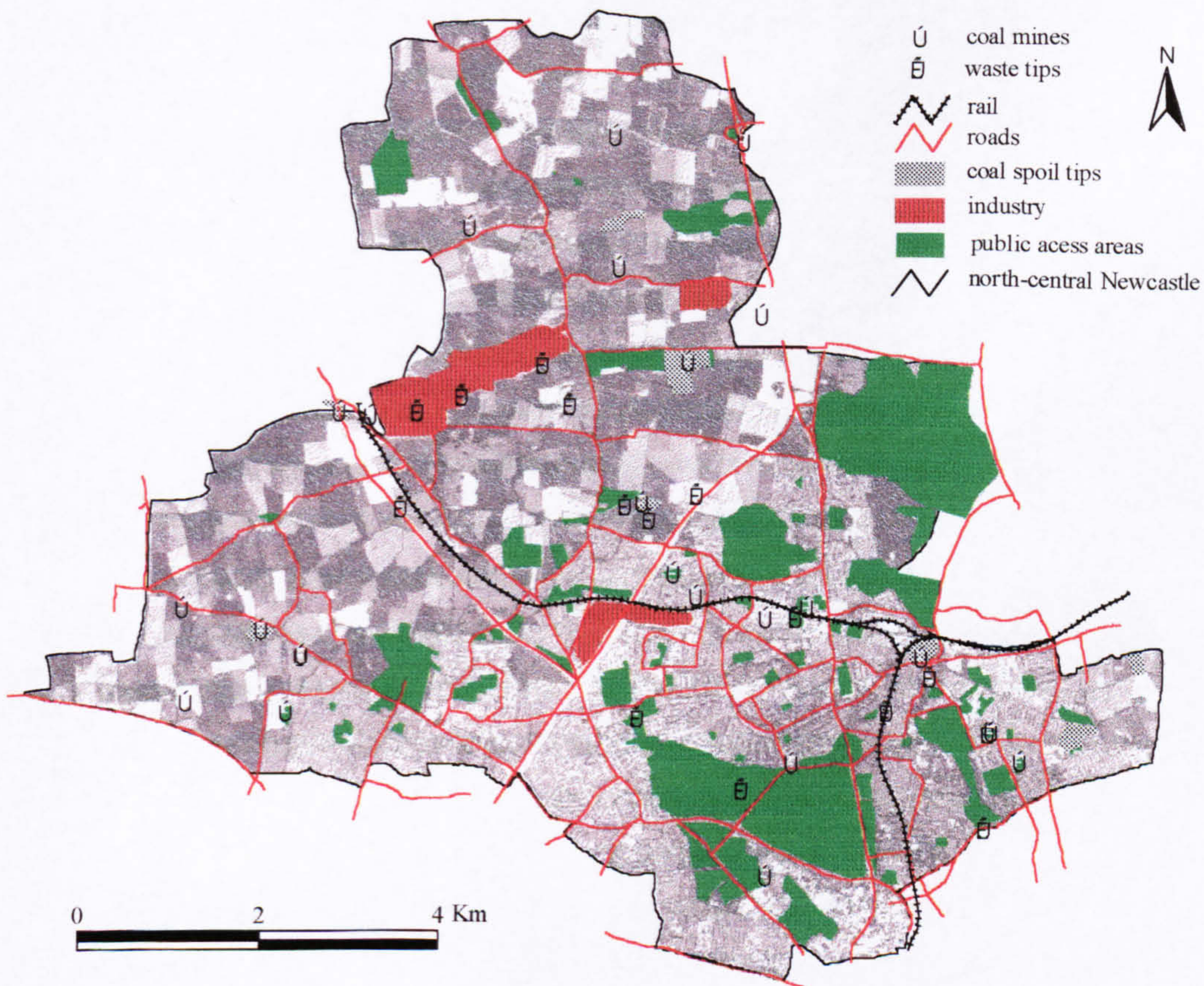


Figure 3.3 Historical industry in north-central Newcastle.

A number of other industries have been historically located within the north-central Newcastle region. A quarry was worked at Kenton for 700 years, providing a valuable source of sandstone for the area. The quarry was finally filled in and grassed over during the 1950s when a substantial part of Kenton was demolished; all signs of the industries (coal mining and quarrying) that dominated Kenton for several centuries have

now gone (Palmer, 1993). Coxlodge was also the site of a quarry during the 1800s (Welford, no date) (Figure 3.3). The other main industries historically located within the region are: potteries, glasshouses, brick works, mills, printers and publishers, chemical and alkali producers, metal manufacturers and smelters and ship builders (Austin, 1992; Austin and Buswell, 1992). At Byker just south of the study area, the base of the tower of the Pb smelting works remains as a monument of this past industry. A number of waste tips, both regulated and unregulated have also been identified within the area (Figure 3.3).

3.2 PREVIOUS STUDIES: HEAVY METAL CONTAMINATION

Previously two studies have investigated the distribution of soil heavy metal contamination within the Tyneside region including north-central Newcastle. Aspinall *et al.* (1988) investigated Pb, Zn and Cd contamination in the metropolitan districts of Newcastle, Gateshead and North and South Tyneside (Section 3.2.1), and Mellor and Bevan (1999) studied Pb contamination in the Ouseburn catchment (Section 3.2.2). Both studies investigated patterns of contaminant distribution and variation, sampling topsoil of public access areas at $1 \times 1\text{km}$ and $200 \times 200\text{m}$ grid scales, respectively. Summaries of the two studies have been included within this chapter as they provide important background information regarding heavy metal contamination within the north-central Newcastle area.

3.2.1 Aspinall *et al.* (1988)

Aspinall *et al.* (1988) collected 412 topsoil samples from relatively undisturbed grassy areas of public open space, to analyse for total and plant available or chemically active Pb, Zn and Cd. Analysis was conducted using AAS, following extraction with nitric and acetic acids, respectively. Metal concentrations were used to determine uncontaminated / contaminated thresholds for soils in Tyneside using a graphical estimation outlined by Davies (1983) (Table 3.1).

	total (mg/kg)	plant available (mg/kg)
Cd	1	-
Pb	80	14
Zn	345	11

Table 3.1 Uncontaminated / contaminated thresholds for Cd, Pb and Zn within soils of Tyneside (Aspinall *et al.* 1988).

Point soil data were aggregated into 1981 census wards and the number of people living in metal contaminated areas estimated for the first time in a major British city. Chloropleth maps of mean concentrations, calculated on a ward basis, were used to identify variations in soil metal contamination across the area. Only general comparisons were made, as the authors were aware of the limitations of this technique. They noted that mean values might not be completely representative of all points within wards and that problems may arise where wards contained radically different numbers of points. Metal concentrations were classified according to legislative guidelines (Appendix 1) and the above threshold values.

Soils of Tyneside were found to contain variable concentrations of Pb. 69.1% of samples, spread throughout the city, displayed concentrations greater than the 80mg/kg threshold, with 35.4% of these samples, located mainly within central Newcastle and along the River Tyne containing between 150 – 550mg/kg of Pb. A number of wards, Elswick, Walker, Harlow Green, Wrekenton and Team Valley, scattered throughout the area, contained samples with concentrations >550mg/kg; these totalled 6.5% of the samples analysed (Figure 3.4). Soil Zn concentrations were less variable with only 14.4% of samples containing >300mg/kg. These samples were widely distributed throughout Tyneside, although there was a tendency for clustering around the River Tyne, especially in the ship building areas of Jarrow, Hebburn and Walker, and near Derwenthaugh (Figure 3.4).

Soil Pb and Zn concentrations displayed distinct geographical patterns which could be related to past and present industry on Tyneside, the greatest contamination being found along the River Tyne, the industrial heartland. Within Gateshead contamination was associated with waste incinerators and other modern industrial operations. Spatial distribution of Pb was seen to bear some relationship to the road network. The study

emphasised the need for further, more detailed investigations into metal contamination in soils of other major conurbations in the UK, as well as the need to examine in more detail the contaminated 'hot-spots' of Tyneside. The authors concluded that future work should seek to ascertain the chemical forms of trace metals in soils as they have major implications for understanding and predicting metal transfer.



Figure 3.4 Wards of Tyne and Wear.

3.2.2 Mellor and Bevan (1999)

To investigate the severity, spatial distribution and potential mobility of topsoil (0–10cm depth) Pb contamination within the Ouseburn catchment, Mellor and Bevan (1999) collected nearly 300 samples from public access and amenity areas. They analysed, using AAS, for total and plant available Pb, following extraction using a

microwave digestion technique (nitric and hydrochloric acids) and a standard acetic acid extraction, respectively.

The study determined that the highest concentrations of soil total Pb were located within urban, central and southern parts of the catchment with a long and complex history of urban and industrial development (Figure 3.5). The lowest values, <200mg/kg, were associated with the rural western and northern regions. In addition, spatial variation was also apparent at a local scale often in the form of contamination ‘hot-spots’ with single high values surrounded by others of relatively low Pb concentration (Figure 3.5). The sample displaying the maximum total Pb concentration, >5000mg/kg, was collected from a small (1ha) green space located within a housing estate in South Gosforth. High values were also found on the Town and Nuns Moors, at Gosforth Park, along Jesmond Vale and at Hazelrigg nature reserve (Figures 3.5 and 3.6). The plant available fraction, which made up on average 10% of the total Pb, displayed similar spatial patterns, with the highest concentration (≈650mg/kg) again located in South Gosforth.

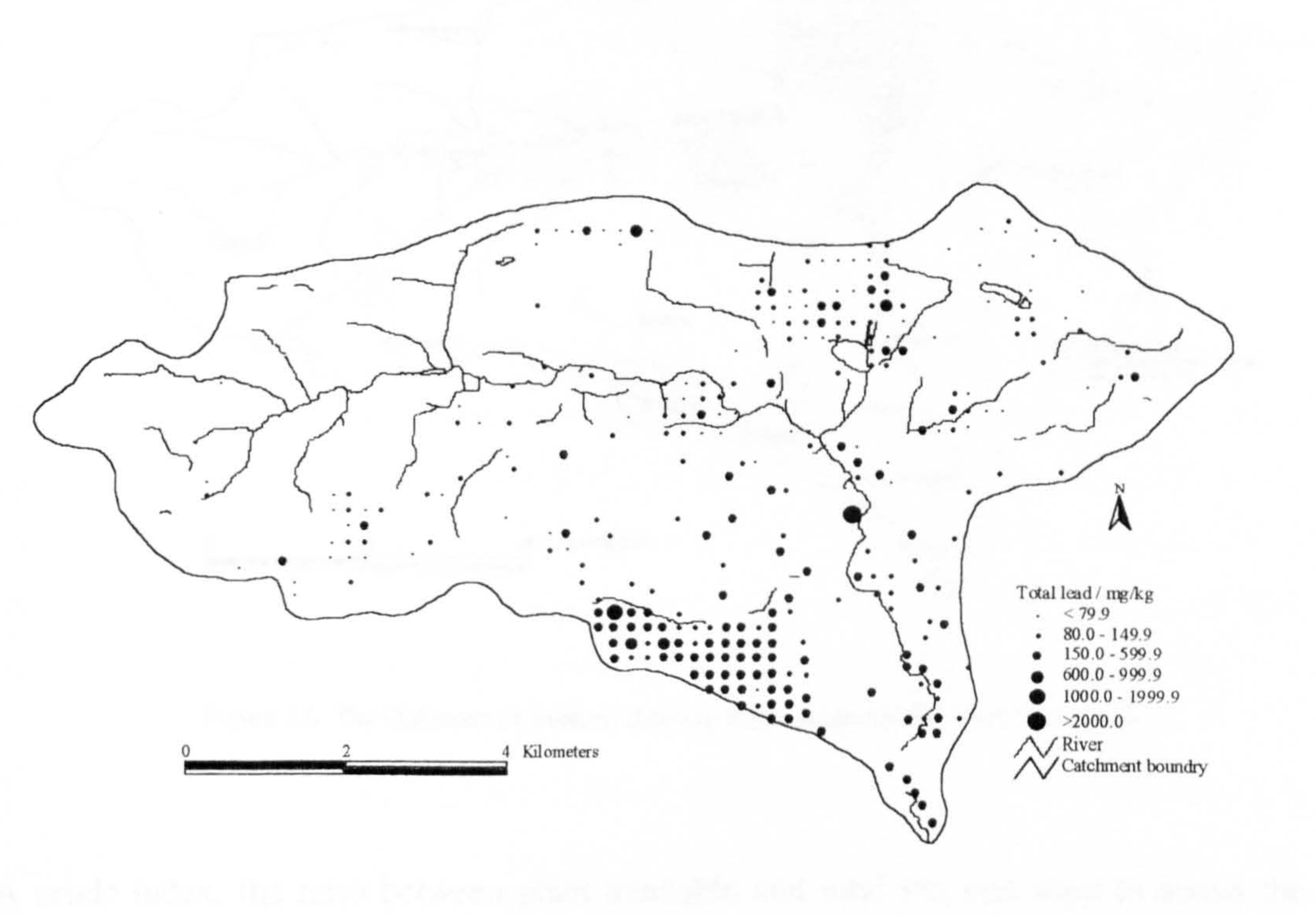


Figure 3.5 Concentration of total Pb, top soil of public access areas, Ouseburn catchment
Adapted from Mellor and Bevan (in press)

In an assessment of severity of the contamination, the authors compared soil Pb concentration to a number of guideline and threshold values. These included (a) the highest probable threshold for uncontaminated soil in Tyneside, 80mg/kg, (Aspinall *et al.* 1988, Section 3.2.1), (b) the British ICRL (1987) guideline for parks, playing fields and open space (2000mg/kg) and (c) the Dutch ABC values (50mg/kg, 150mg/kg and 600mg/kg,) (Appendix 1). 72% of the samples contained concentrations greater than Aspinall's threshold, displaying higher than background levels of Pb. Only one sample exceeded the British guideline, whereas approximately 33% exceeded the Dutch B value (indicative of further investigation), with almost 2% exceeding the Dutch C value (clean up threshold). The severity of contamination was therefore seen to be dependent on the guidelines chosen.

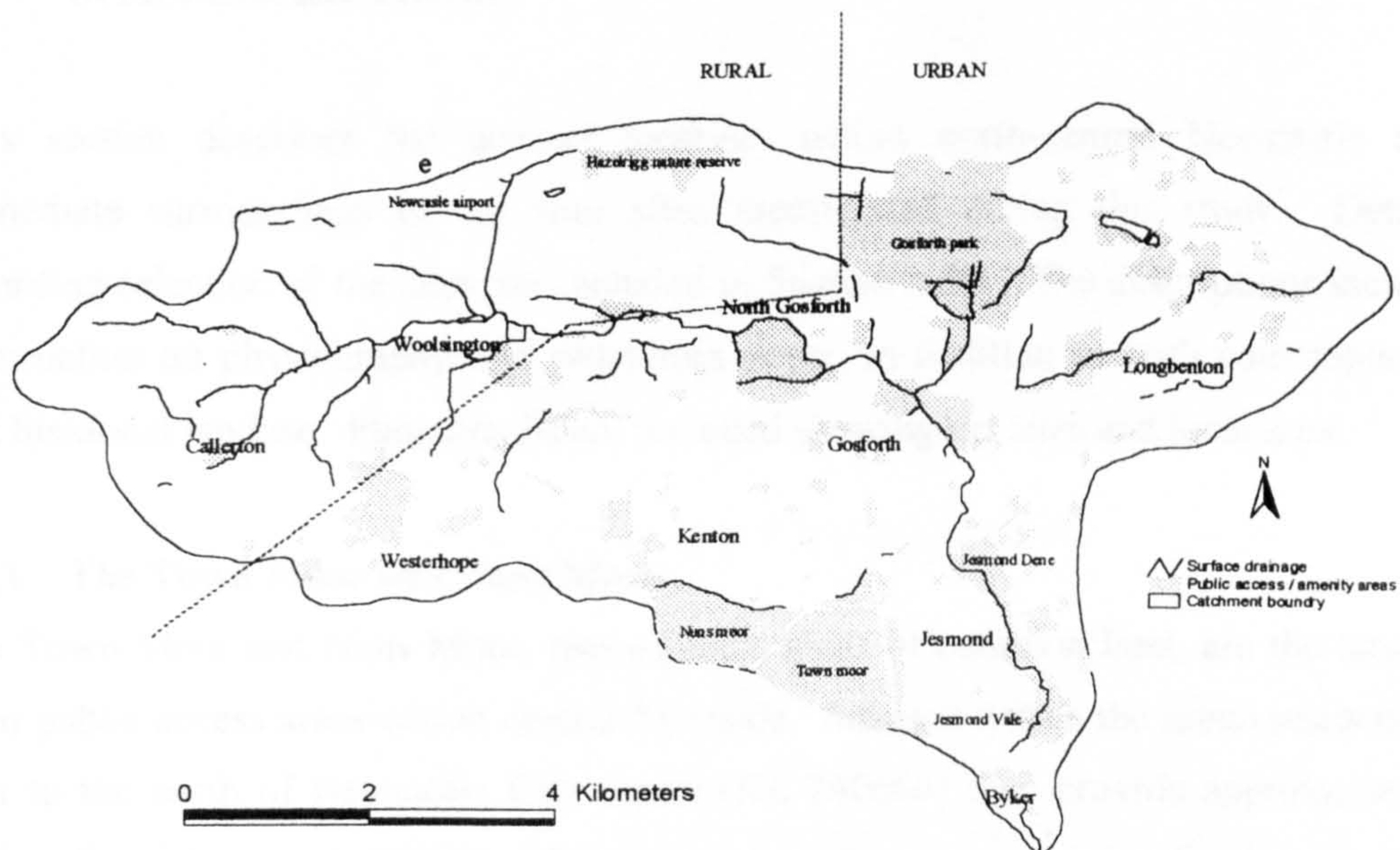


Figure 3.6 The Ouseburn catchment, showing major areas and the urban rural divide.

A crude index, the ratio between plant available and total Pb, was used to assess the potential mobility of Pb within the soil. These ratios displayed very different patterns of spatial distribution than either the total or available fractions, possibly reflecting different sources of contamination. The northern and western regions, as well as the Town and Nuns Moors, displayed the highest ratios. The authors concluded that Pb in

rural regions may be more soluble and mobile due to its tendency to be derived from weathering and related pedological alteration. In the urban environment Pb was dominated by less mobile and more persistent forms, the sources of which were industrial and urban activity.

The authors highlighted the need for more detailed research into the behaviour and mobility of metals within the soil system, suggesting the need for investigations into speciation and partitioning, as well as a range of soil properties considered to affect mobility. With regard to the interpretation of spatial patterns they noted the effect of sampling density on the conclusions drawn.

3.3 SITE DESCRIPTIONS

This section describes the general location, within north-central Newcastle and immediate surroundings of the four sites investigated during this study. Details regarding selection of the sites are included in Section 4.2.1. The descriptions include information on physiography and vegetation cover, in addition to both contemporary and historical landuse. Photographs are included showing the sites and local area.

3.3.1 The Town Moor and Nuns Moor

The Town Moor and Nuns Moor, two adjacent areas of common land, are the largest open public access areas within central Tyneside. Situated within the urban residential area to the north of Newcastle City centre (NZ 240660) they provide approximately 260ha of mainly open grassland. The sites are important amenity areas for the city used by dog walkers, runners, cyclists, trail bikers and radio controlled plane enthusiasts.

The town moor is of largely flat relief however, two small manmade hills, a legacy from construction of the A167(M) central motorway, form the south western corner. The moor slopes gently down towards the northern edge of the site that is bounded by a tributary stream during the wetter winter months. Apart from a few small clusters of deciduous trees located along the southern boundary and south western corner vegetation cover is characterised by scrub type grass species. The grass is kept relatively short by occasional mowing in addition to the grazing of cattle throughout the

spring and summer months. The moor is crossed by a number of tarmac paths that form the main routes across the site. A degree of vegetation wear is noted in the vicinity of these paths during dry summers. The eastern edge of the Town Moor is the site of the annual 'Hoppings' fun fair in mid to late June, an event that results in substantial vegetation wear and exposure of bare soil. Contamination of soil as a result of minor fuel spillages from fair ground vehicles and generators is a possibility (Plates 3.1 – 3.3).



Plate 3.1 Aerial photograph of the Town Moor and Nuns Moor.

The Nuns Moor site, despite its proximity to the Town Moor exhibits a notably different topography. The area divided into two different landuses, open amenity land to the north and a golf course to the south, displays a number of interesting features. The golf course is of generally flat relief whilst the public access land slopes down towards the northern boundary of the site. This area exhibits a ridge and furrow micro-topography thought to remain from its historic use as agricultural land. Signs of site disturbance to the east can be identified by close examination of aerial photographs. On the whole, the site is characterised by grassland vegetation although a number of deciduous trees have been planted on the golf course. Like the Town Moor the Nuns Moor is grazed by cattle, throughout the spring and summer, keeping the grass relatively short. The golf course on the other hand undergoes continual maintenance. A small tributary stream forms the northern boundary of the site, within the vicinity of which soil can become

quite waterlogged under wet conditions. Some bare patches of soil exist, located mainly in the vicinity of the site access points, footpaths and close to the stream (Plates 3.1, 3.4 and 3.5).



Plate 3.2 The Town Moor looking east towards Jesmond, showing the hoppings fun fair.

The busy A167(M) central motorway, forms the southern boundary of the two moors, with other main link roads encompassing the Town Moor. Residential housing estates form the northern and western boundaries of the Nuns Moor. Historically the Town Moor has been the location of a racecourse and small pox hospital, as well as a site for the disposal of excess material during the construction of the central motorway. The north-eastern area of Nuns Moor was used as a waste disposal site during the 19th century and evidence of old ridge and furrow suggests the north western corner has previously been used as agricultural land.



Plate 3.3 The Town Moor, looking north.



Plate 3.4 Nuns Moor looking north towards Kenton.



Plate 3.5 Newcastle Golf Course, taken looking south from Nuns Moor.

3.3.2 Hazelrigg nature reserve

Hazelrigg nature reserve, located in the northern rural region of north central Newcastle (NZ 220710), is adjacent to the villages of Hazelrigg and Wideopen, within close proximity to Newcastle International Airport. The part wooded, part open area provides approximately 40ha of land for recreational purposes. The area is used extensively by children, particularly during the summer months, in addition to dog walkers, horse riders, cyclists and bird watchers. Historically the site provided a colliery spoil tip for the local coal pits having only recently been reclaimed to form the nature reserve.

The eastern side of the site, the old spoil tip, is characterised by wooded vegetation, consisting of both deciduous and coniferous tree species. The trees recently planted following reclamation of the site are relatively young. The area exhibits a dome shaped topography rising from all directions to an approximately central point. Several drainage ditches run north to south through this area. Adjacent to the woodland lies the second main area of public access land at this site, an area of flat relief, characterised by relatively poor vegetation cover. Here vegetation includes grasses, shrubs and some deciduous trees, in addition to number water loving species surrounding the two surface

water bodies. Deciduous trees also line the main spoil footpath along the northern boundary of the site. Patches of bare soil are not uncommon at the site particularly in the vicinity of footpaths and access points (Plates 3.6 –3.8).

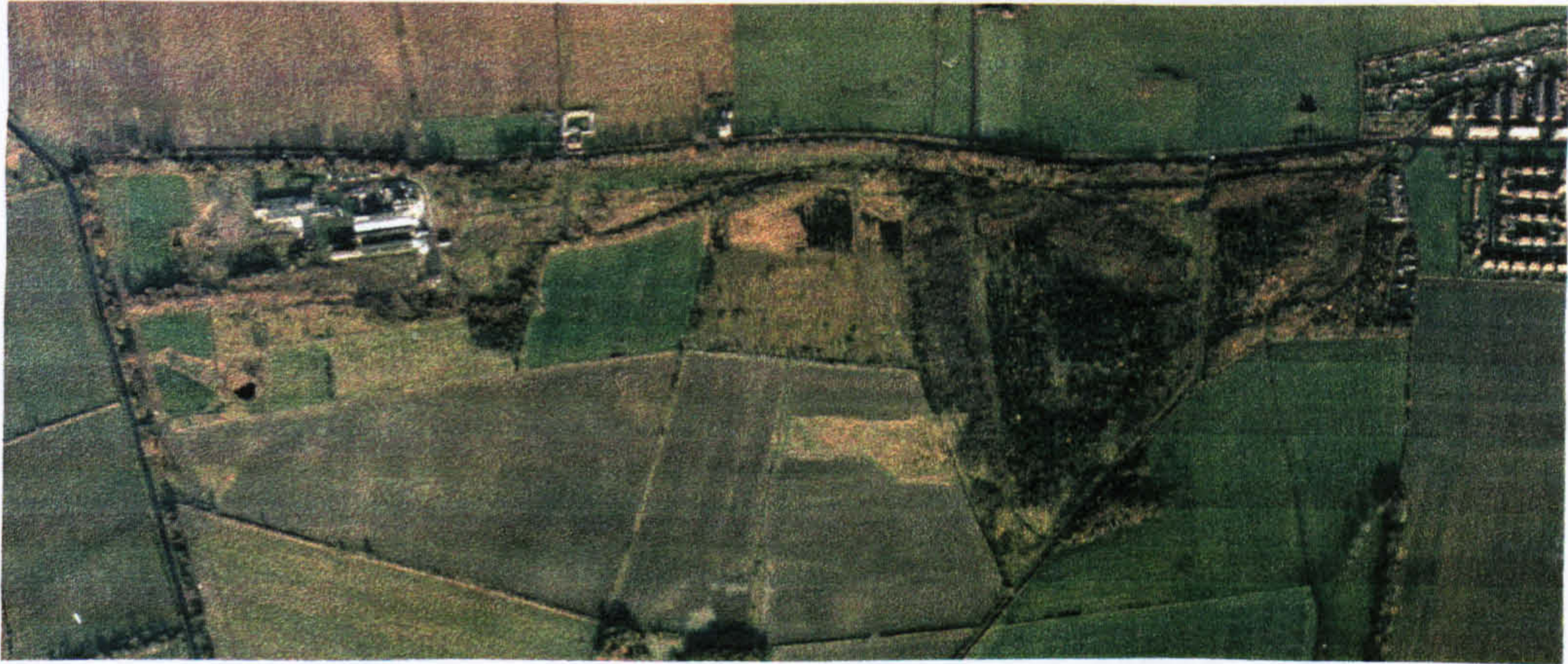


Plate 3.6 Aerial photograph of Hazelrigg nature reserve.



Plate 3.7 Hazelrigg nature reserve, open area.



Plate 3.8 Hazelrigg nature reserve, wooded area.

3.3.3 South Gosforth

The South Gosforth site, located within the urban residential area of South Gosforth (NZ 254682) is a small region of grassland approximately 1ha in size. The area, surrounded by housing, mostly flats with little or no gardens, provides an important open space for the surrounding residences. The land is predominantly used by children and for the exercising of dogs. The area of virtually flat relief is maintained by the local council who keep the grass short by regular mowing throughout the growing season. The site is bordered to both the south and east by young deciduous trees and shrubs

Historically South Gosforth was a coal mining area, being the location of two of the regions largest pits. Capped pit shafts remain as a reminder of the area's mining history, one being located approximately 10m north of the site. The area of dead grass shown by the aerial photograph (plate 3.9) is thought to be the site of a bonfire, however the grass has now regenerated and the site no longer visible.



Plate 3.9 Aerial photograph of the South Gosforth site.



Plate 3.10 South Gosforth site, looking north west.



Plate 3.11 South Gosforth site, looking north.

CHAPTER 4

METHODOLOGY

Summary

This chapter outlines the methodology, theory and assumptions and justifies the choices made during the planning, collection and analysis of data for this investigation. The chapter has been divided into 6 sections, ordered from initial sampling design to final data analysis. Section 4.1 introduces the project providing background information and setting the scene for the new investigation. Issues regarding sampling design, including site selection and sampling strategy are outlined in section 4.2. Laboratory analyses are outlined in section 4.4, these include sample pre-treatment, heavy metal extraction and analysis and soil property determination. Analyses, in addition to sample collection are fully described in Appendix 2. Issues of quality assurance and quality control are raised in section 4.4. A detailed description of the quality control conducted on the metal extraction techniques is included in Appendix 3. Sections 4.5 and 4.6 outline the data analysis techniques used, including exploratory data analysis, geostatistical techniques, principal components analysis and non-hierarchical classification. Statistical theory and assumptions are expanded within Appendices 5-9.

4.1 INTRODUCTION

Mellor and Bevan (1999) examined top soil Pb contamination within the Ouseburn catchment, Tyneside, on a finer geographical scale than had previously been investigated. The study identified a high degree of spatial variation across a sampling grid of $200 \times 200\text{m}$. Although contamination appeared to be localised, displaying a hot spot pattern of distribution, it exhibited a clear urban / rural divide, with urban sites having consistently higher metal concentrations. More specifically, higher levels of Pb could be identified at sites associated with reclaimed colliery spoil or waste disposal activities. A number of areas within the catchment displayed interesting spatial patterns of soil Pb contamination. Similar patterns were associated with Zn contamination within the catchment (Mellor and Bevan, unpublished), although on the whole Zn concentrations were lower and less variable.

This project will examine a number of these areas, looking at the spatial variation of Pb and Zn on an even finer geographical scale. Plot sites of topsoil contamination, ranging from $200 \times 150\text{m}$ down to $5 \times 5\text{m}$ in area will be investigated using a geostatistical

approach, involving variograms and kriging to examine spatial dependence and produce surface interpolations, respectively (Chapter 5). Sequential extractions, conducted on soil samples collected from a plot site, will be used to establish the partitioning of the metals within the system (Chapter 6) and hence make inferences regarding their fate, mobility and bioavailability (Chapter 7).

4.2 SAMPLING DESIGN

4.2.1 Site selection

Previous studies, conducted both locally within Tyneside (Aspinall *et al.*, 1988; Mellor and Bevan, 1999) and further afield (Douglas *et al.*, 1993; Merrington and Alloway, 1994; Rieuwerts and Fargo, 1995; Kelly *et al.*, 1996) have identified urban sites where the soil is contaminated with heavy metals. Many of these sites are associated with past or present industrial operations such as mining and smelting, urban development and waste disposal, or are located adjacent (50 – 60m) to roads (Albasel and Cottenie, 1984, Jaradat and Momani, 1999). Soils of urban parklands, when compared to their rural counterparts, have been identified as exhibiting elevated concentrations of heavy metals (Purves and McKenzie, 1969; Douglas *et al.*, 1993) (Section 2.3). Such public open spaces provide important recreational facilities for a relatively high proportion of the urban population, and contamination at these sites therefore poses a high degree of hazard. Research has shown children to be most at risk from Pb contamination (Oliver, 1997) raising concerns regarding the environmental quality of areas in which they reside and play (Section 2.2).

A number of site selection criteria were developed in line with the main aims of the thesis (Section 1.2) and with reference to previous relevant studies, notably that of Mellor and Bevan (1999) which covered approximately the same geographical area as this investigation (Section 3.2.2). Suitable sites were to be:

1. Public access and amenity areas such as parks, playing fields, open green spaces etc.
The contamination of such areas is of relevance to a large cross-section of the community, particularly children who are thought to be most at risk.

- 2. Characterised by higher than background concentrations of heavy metals and / or interesting spatial patterns as the project aims to investigate the behaviour of heavy metals in soils and the spatial variation in levels of contamination.
- 3. Areas which had previously been disturbed, previous studies having identified such areas as likely candidates for soil contamination.

Initially, four sites were selected, although all three criteria were not satisfied at each site (Table 4.1). The areas chosen for the initial study are highlighted on Figure 4.1.

sites	site description	1	2	3
South Gosforth	1 ha grassland site within residential area	✓	✓	✓
Town moor	Grassland site, centre of Town moor	✓	✓	?
Nuns moor	Grassland site, north west edge of Nuns moor	✓	✓	?
Hazelrigg	Reclaimed colliery spoil, part wooded part grassed	✓	✓	✓

Table 4.1 Sites chosen for further study, including a brief description and an indication of the site selection criteria met.

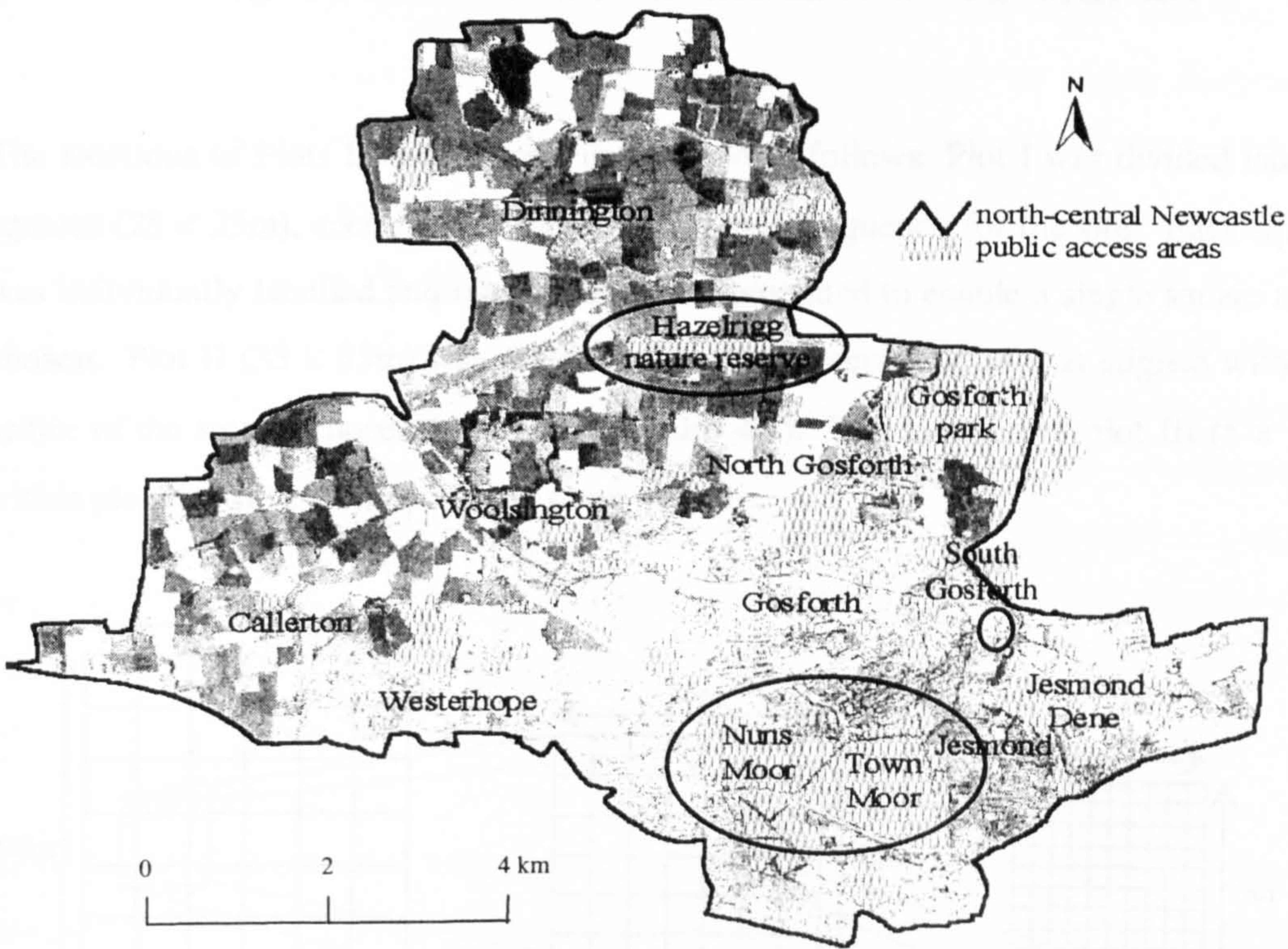


Figure 4.1 Location of chosen sampling sites

From the initial study a plot site (plot I), selected from an area of heavy metal contamination on Nuns moor, was chosen for a more detailed investigation. This study examined both the spatial variation and the forms of the metals (Pb and Zn) within the soil. Geostatistical analysis of spatial patterns of the metals within plot I ($150 \times 200\text{m}$) identified the need for sampling on a finer scale. Two further plots, plot II ($35 \times 35\text{m}$) and plot III ($5 \times 5\text{m}$), were therefore randomly chosen from within plot I thus allowing the full extent of Pb and Zn spatial dependence to be determined (Figure 4.2).

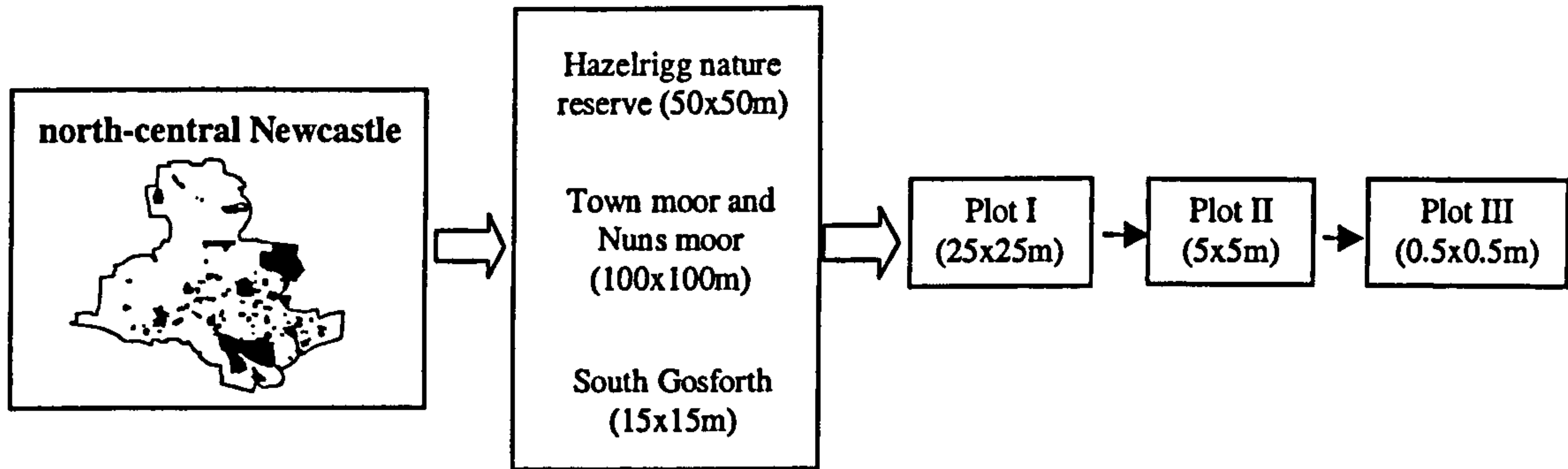


Figure 4.2 Diagrammatic representation of site selection indicating sampling scales

The locations of Plots II and III were determined as follows: Plot I was divided into 48 squares ($25 \times 25\text{m}$), according to the sampling grid frequency for the site. Each square was individually labelled and random numbers generated to enable a single square to be chosen. Plot II ($35 \times 35\text{m}$) was orientated so that its centre point was aligned with the centre of the square chosen from plot I (Figure 4.3). The location of plot III ($5 \times 5\text{m}$) within plot II was determined in the same manner.

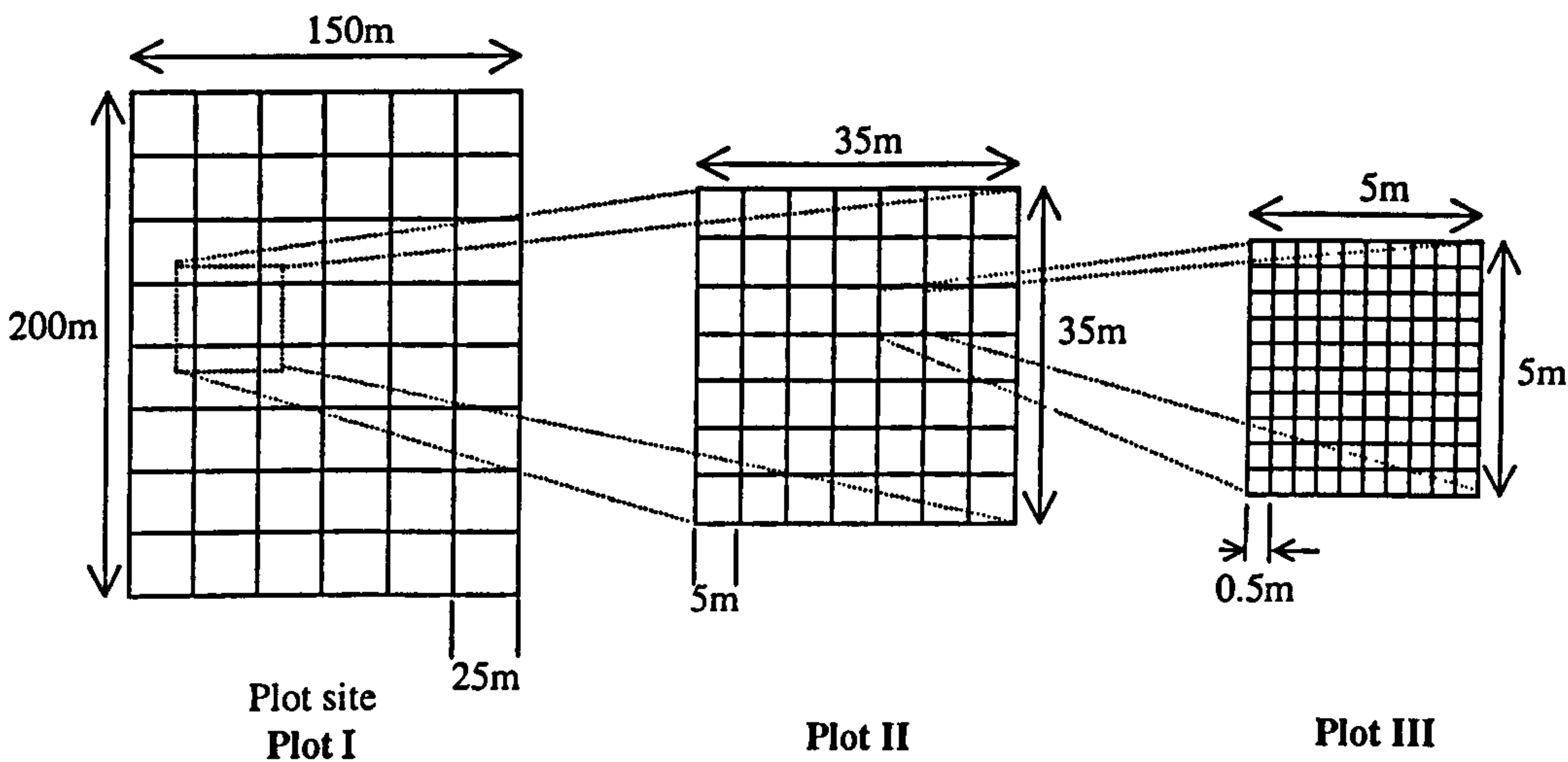


Figure 4.3 Location of plots II and III within plot I

4.2.2 Sampling strategy

Ferguson (1992) stressed the importance of appropriate sampling design when conducting a site survey on potentially contaminated land. He emphasised that a poorly designed sampling strategy or sparse sampling may lead to the non-identification of contaminated areas within a site. Site survey is a balance between resources, for example time and money, and the need to generate the highest possible probability of locating contaminated areas. The aim is therefore to design an optimum sampling strategy that furnishes a sufficient but not excessive number of data points to characterise a contamination problem (Schweitzer and Black, 1985). Statistics play a vital role in strategy development and can effectively be utilised in determining the required frequency of sample point locations. Spatial sampling strategies assume that within a site all points have an equal chance of containing a hot spot (Ferguson and Abbachi, 1993).

Three main sampling patterns exist for use in site survey, the regular grid or systematic sampling pattern, stratified random and random (Figure 4.4). All three patterns have advantages and disadvantages. Random patterns, for example, whilst avoiding bias, may lead to problems such as clustering of sample points and / or sparse sampling in particular areas. The regular square grid is the most commonly used strategy, displaying obvious practical advantages in being easy to set out in the field. Sampling in this way also allows the whole survey area to be evenly covered, although alignment of sample locations reduces the ability of the strategy to identify elongate targets, particularly if they are located along the axes of the grid. The herringbone sampling pattern, designed by Ferguson (1992), whereby samples are slightly yet consistently unaligned (Figure 4.4), exhibits increased performance at identification of elongate targets. In this investigation however a systematic grid sampling pattern was chosen to survey all soil sites. Such a pattern is normally used when attempting to evaluate spatial variation of soil contaminants (Bruner, 1986).

Sampling point frequencies were chosen independently for each of the 4 study areas (for area locations see Figure 4.1), the sample grid spacing being determined in order to generate an appropriate number of sampling locations given available resources. Results from sampling of study areas were used in the identification of a plot site (plot I) of contaminated land at which investigations into the forms and behaviour of metals

were conducted. The sampling strategy employed could therefore be described as multi-stage, with information from the first sampling stage being used in the choice of location for the second sampling stage - plot I. As a contaminated site was required for this study, it was essential that the efficiency of study area sampling networks at locating contamination hotspots were assessed.

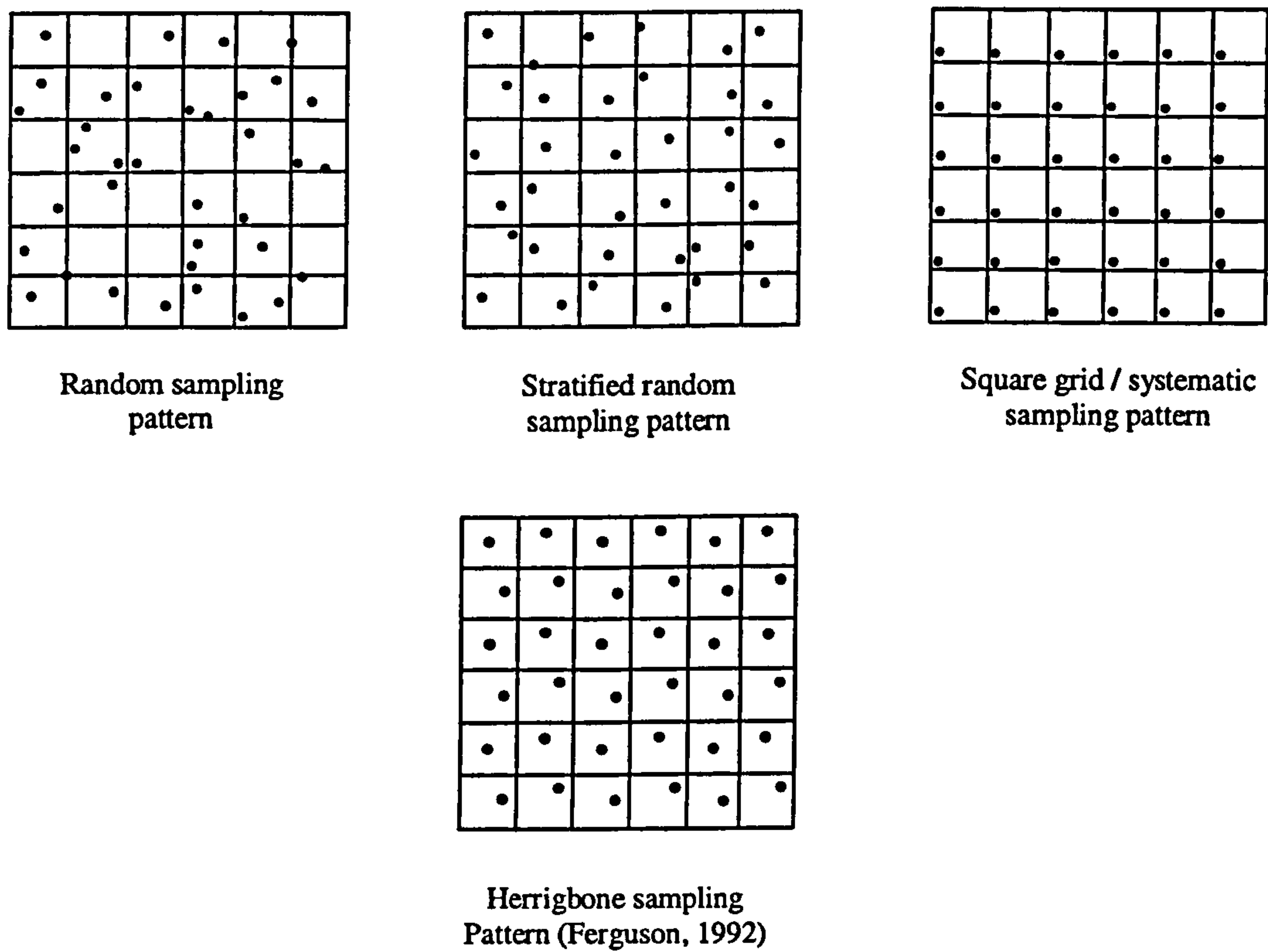


Figure 4.4 Diagramatic representation of the most common sampling patterns

In order to assess the probability of the sampling missing a contaminated hotspot, i.e. sampling efficiency, if a hotspot were to exist, a technique described by Zirschky and Gilbert (1984) was employed. The technique utilises the computer program ELIPGRID originally designed to evaluate geologic deposits. The program enables an assessor to calculate the probability with which a given sampling pattern of known frequency will miss a contaminated hotspot of a certain shape and area, given that contamination has been defined. Here, as public access areas were being surveyed, soil was defined as being contaminated with the metals Pb and Zn if it contained >2000mg/kg and or

>300mg/kg respectively, in line with the current UK ICRCL (1987) guidelines¹ on contaminated land (Appendix 1).

The acceptable risk or probability, B , (also defined as public risk by the authors) of the given sampling pattern and frequency not identifying a contaminated hotspot is calculated as follows. The size and shape of the target hotspot are defined by its semi-major and semi-minor axes, L and l , respectively, with S the shape of the hotspot being defined by the ratio of l to L . S is therefore 1.0 for a circular and < 1.0 for an elliptical target. B is calculated using the graph shown in Figure 4.5, where G is the spacing between sampling points (Zirschky and Gilbert, 1984). The chosen sampling frequencies for each of the study areas and plot sites are shown below (Table 4.2). Table 4.3 indicates the size (L) of contaminated hotspot each site sample spacing (G) (Table 4.2) will fail to locate, assuming an acceptable risk (B) and hotspot shape (S). Hotspot size was determined using Figure 4.5. This method enabled the author to determine the size of contaminated hotspot liable to be missed by the chosen sampling strategies. Soil samples were collected following the strategy outlined in Appendix 2.

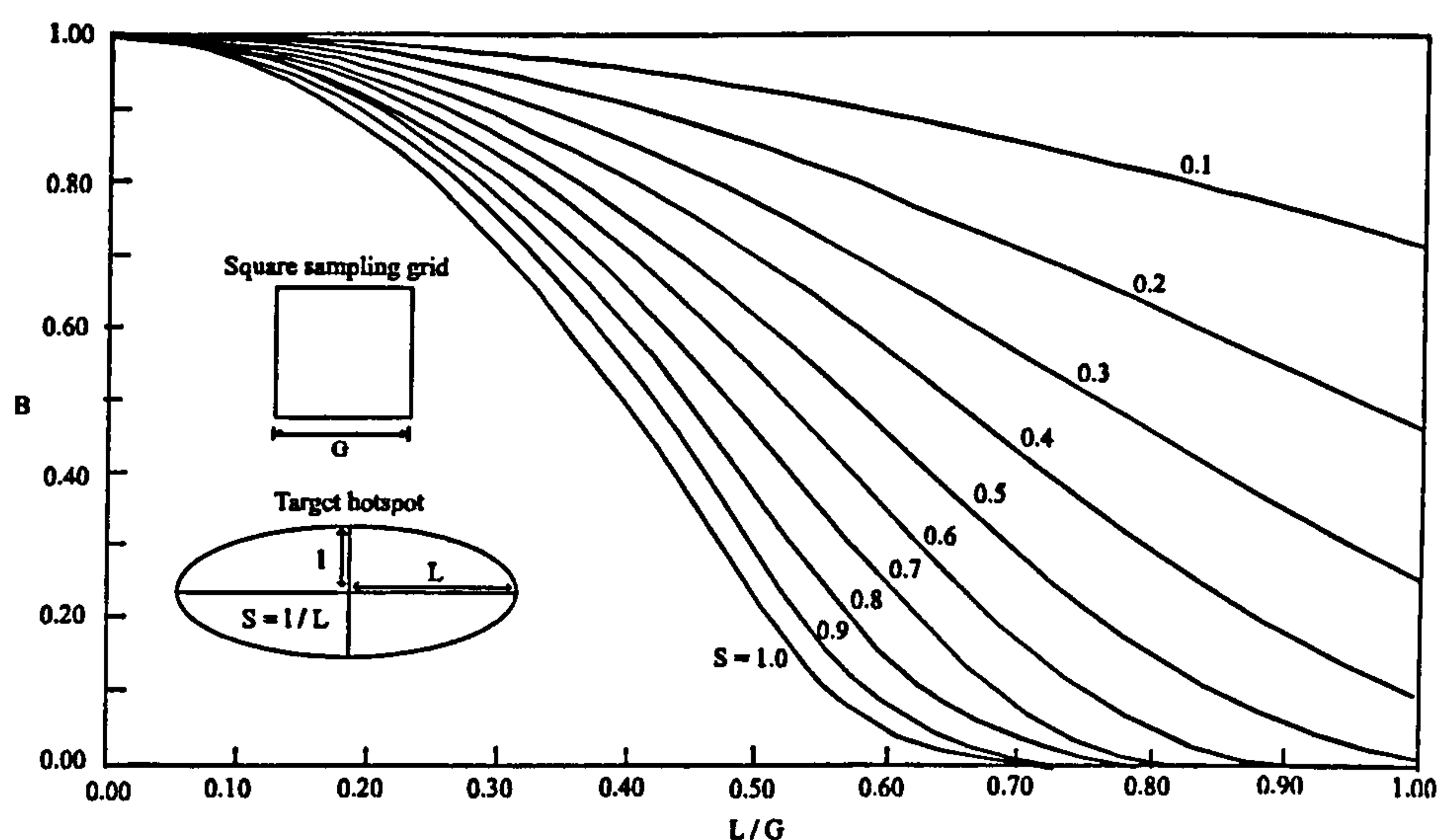


Figure 4.5 Probability, B , of sampling procedure missing the specified target vs. ratio of target's semi-major axis to square-grid spacing for various elliptical targets. Adapted from Zirschky and Gilbert (1984).

¹ ICRCL guidelines specify trigger values dependent on both the contaminant and land use. No trigger value exists for Zn within parks, playing fields and open spaces, hence the value for any land where plants are to be grown has been used here (Appendix 1).

study area		sample grid spacing (m)	no. of sampling points
Gosforth		15 × 15	35
Town Moor		100 × 100	32
Nuns Moor		100 × 100	19
Hazelrigg nature reserve -	open	50 × 50	27
	wooded	50 × 100	24
Plot site – Nuns Moor –	Plot I	25 × 25	63
	Plot II	5 × 5	64
	Plot III	0.5 × 0.5	121

Table 4.2 Sample spacing for chosen study areas

S	B	G = 15m	L (m). where	
			G = 50m	G = 100m
1.0	0.01	9.8	32.5	65.0
	0.05	8.8	29.3	58.5
	0.10	8.4	28.0	56.0
0.5	0.01	14.9	49.5	99.0
	0.05	13.5	45.0	90.0
	0.10	12.9	42.0	84.0

Table 4.3 Probability, B, with which the chosen sampling frequencies, G, will fail to locate contamination hotspots of given size, L, and shape, S, if they were to exist

4.3 LABORATORY ANALYSIS

Good laboratory practice was observed during all analytical procedures, with standard techniques employed wherever possible (Appendix 2). A rigorous programme of quality control was developed to assess both the reproducibility and efficiency of any non-standard methodology: this programme, described in Appendix 3, was maintained throughout the analytical process. Class A glassware was used and where appropriate analytical grade chemicals and de-ionised water. All equipment used in the extraction and analysis of heavy metals was acid washed overnight in 5% nitric acid and thoroughly rinsed in distilled water. Care was taken to ensure that all equipment was made of suitable material to avoid heavy metal contamination and reduce losses due to adsorption onto its surfaces. All the analytical techniques and methods employed are outlined in Appendix 2.

4.3.1 Heavy metal extraction

Two methods were employed in the extraction of heavy metals from the soil samples: a total digest using a microwave extraction and a sequential extraction using the BCR technique, as specified by Davidson *et al.* (1994) (Appendix 2). Build up of pressure inside the microwave digestion containers allows the temperature to rise above normal boiling point, hence reducing extraction time to approximately one hour, a substantially reduced time compared to that of the standard overnight block digest. The BCR sequential extraction technique, the standard method of the European Community Bureau of Reference, is a well used extraction procedure that may be conducted without specialist equipment.

Rigorous quality control checks proved the extraction techniques to be both reproducible and efficient (Appendix 3). Care was taken to avoid contamination of samples during the extraction and storage processes. Extraction solutions were stored in polyethylene containers in the dark at 4°C until analysis. Sequential extractions were only conducted on samples collected from plot I. All samples were analysed for total metals.

4.3.2 Heavy metal analysis

Extraction solutions were analysed for Pb and Zn using the standard method of flame atomic absorption spectrometry, AAS (Perkin Elmer 2380) (Appendix 2). Again, to avoid contamination, all apparatus was soaked overnight in 5% nitric acid and washed in distilled water. Appendix 4 explains the technical aspects of the instrumentation and operation of AAS. Prior to use, the AAS was optimised and calibrated with a set of known standards, made up using dilution from a high purity, 1000ppm solution. Calibration required three standards, S_1 , S_2 and S_3 . The concentration of S_1 corresponded with the top of the linear absorption range for the metal analysed (Table 4.4), as specified by the manufacturer. S_2 was equal to 3 times the concentration of S_1 and S_3 equalled 2 times the concentration of S_2 . For Pb, for example, $S_1 = 5\text{ppm}$; $S_2 = 15\text{ppm}$ and $S_3 = 30\text{ppm}$. Extractants displaying concentrations above the linear range were diluted and re-analysed to maintain a high degree of accuracy (Appendix 4).

element	wavelength (λ)	slit (nm)	flame gas	liner range (ppm)	sens. check (ppm)
Pb	217.0	0.7	A-Ac	5.0	4.0
Zn	213.9	0.7	A-Ac	0.2	0.5

Table 4.4 Standard conditions for atomic absorption. A-Ac indicates air and acetylene

4.3.3 Soil properties

Current research has identified a number of properties as exerting an influence on heavy metal retention with the soil system (McKenzie, 1980; Sauve *et al*, 1997; Hooda and Alloway, 1998; Rieuwerts *et al*, 1998) (Section 2.6). In general, soil pH, CEC and organic matter content, despite sometimes conflicting results, have been identified as the main properties influencing the mobility of heavy metals (Alloway, 1995). The greatest influence is exerted by pH. Samples collected from plot I were analysed for these properties in addition to metal fractionation. The analysis provided extra information regarding soil Pb and Zn behaviour within the plot. Soil properties were determined using the standard techniques outlined in Appendix 2.

4.4 QUALITY ASSURANCE

The evaluation of quality control within soil sampling requires the determination of precision, accuracy and representativeness at each stage of the sampling programme. Throughout every step correct protocol must be followed, appropriate tools used and equipment properly maintained and calibrated. If these rules are followed errors will be small and data quality assured.

The nature of soil is such that heavy metal contamination tends to be heterogeneous and, therefore, the concentrations of metals associated with individual particles of the same soil sample can vary dramatically (Rubio and Ure, 1993). This non-homogeny of contamination introduces obstacles to accurate sample collection, handling, extraction and analysis. Each step in the process from collection through to analysis requires the physical manipulation of samples and hence introduces a degree of error into the overall result. Sample handling operations include extraction of soil from the ground, drying of the sample, disaggregating and sieving, mixing of the sample to reduce heterogeneity and the extraction process. Each step is essential if precision, accuracy and

reproducibility are to be maintained throughout the data collection process. Unlike analytical error, which may be quantified by quality control procedures, errors caused by the physical handling and manipulation of samples are both difficult to characterise and to control. In order to reduce total error both sampling and analytical errors must be reduced, and this can only be achieved by being aware of the possible causes of such errors within both the field and the laboratory.

Shefsky (1997) defined two major types of sampling error: sampling bias and fundamental error, both of which are measurable and controllable. The author maintains that if all particles in a sampling unit have exactly the same probability of being selected for inclusion in a random sample, a sampling methodology may be considered as being unbiased and correct. In reality bias can only be reduced by the recognition of certain phenomena, such as the tendency for denser particles to settle towards the bottom of a sample and the possible concentration of contaminants in aggregates. An unbiased sample is practically impossible to attain as fundamental sampling error determines that a random sub-sample taken from a sample of fixed mass will never be of exactly the same composition as the original sample. Differences in composition will be randomly distributed, and therefore sub-sampling leads to the introduction of another set of potential errors (Appendix 3).

4.4.1 Possible sources of error within this investigation

Errors, which may be incorporated within the processes of soil sampling and analysis are, summarised in Table 4.5 where they have been divided into 5 main categories. Those introduced during sampling design, sample collection and sample handling were not quantified for this study, although awareness of the possible sources and causes of errors enabled appropriate protocol to be followed and hence quality was maintained. Errors introduced during sample extraction and analysis have been quantified and controlled (Appendix 3).

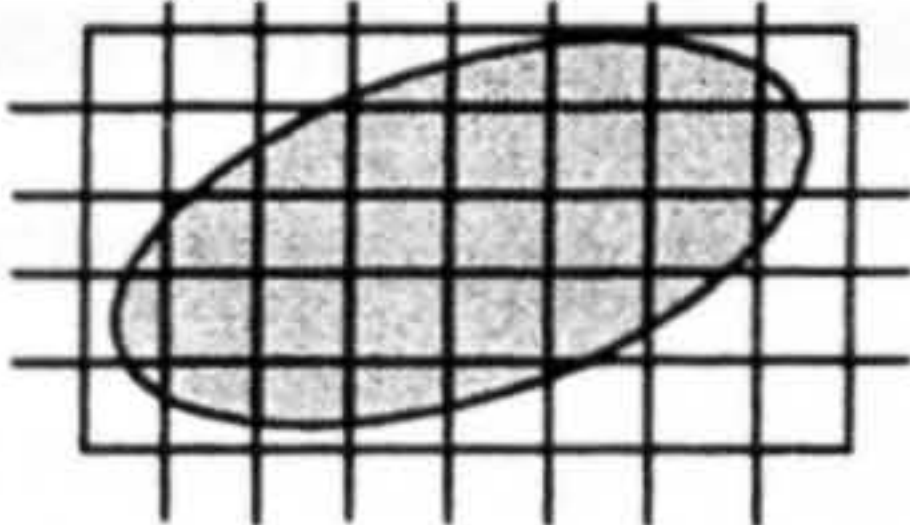


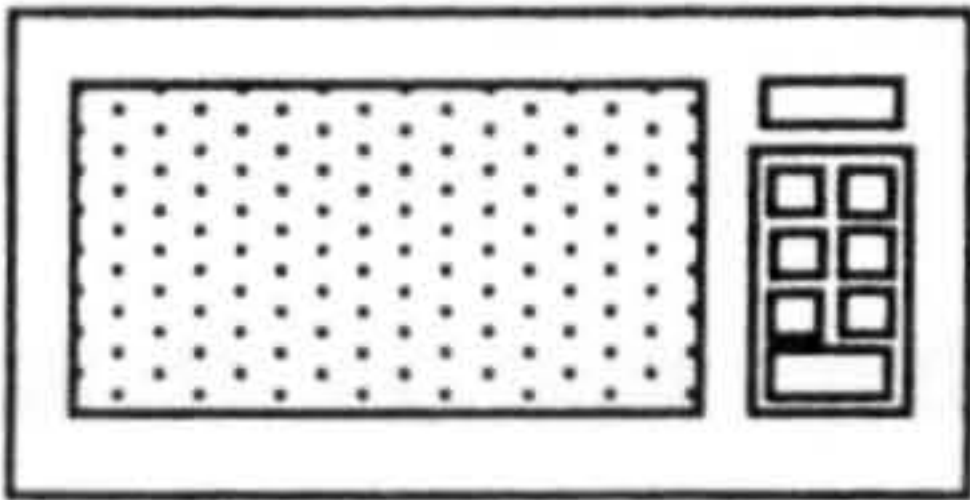
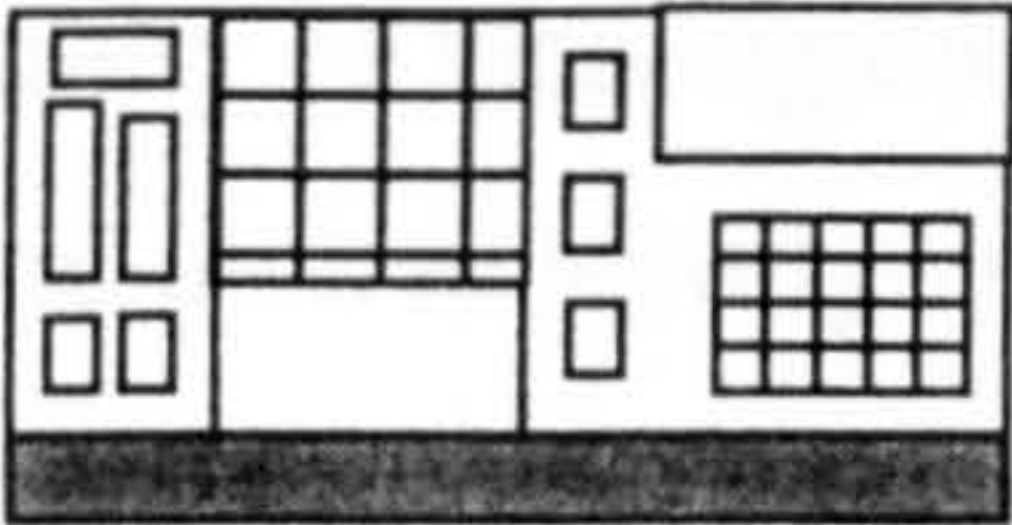
possible sources of error	
<div>sampling design</div> <div></div>	<ul style="list-style-type: none">• non-identification of hotspots of contamination due to sampling design (pattern, frequency, support)• inclusion of non-representative sample locations, i.e. near to obvious sources of disturbance or contamination, e.g. footpaths, fences, lamp posts
<div>sample collection</div> <div></div>	<ul style="list-style-type: none">• mis-identification of sample point locations due to errors in the measurement of direction and distance• cross contamination of samples via the transfer of sampled material on non-clean equipment• contamination caused by the use of sampling tools and storage containers of inappropriate materials• inaccurate labelling of samples
<div>sample handling</div> <div></div>	<ul style="list-style-type: none">• moisture content > 2-3 % of the sample mass following drying• loss of fines during the processes of disaggregation and sieving• cross contamination of samples by the use of non-clean equipment
<div>sample extractions</div> <div></div>	<ul style="list-style-type: none">• lack of sample homogenisation, each grain must have an equal chance of being chosen for extraction• loss of fines• lack of accuracy, e.g. during weighing and measuring• poor chemical and water quality• contamination from containers and glassware <div>quality checks – reproducibility and efficiency</div>
<div>sample analysis</div> <div></div>	<ul style="list-style-type: none">• instrument errors• matrix effects• chemical effects• poorly maintained equipment• calibration errors caused by poor quality standards and blanks <div>quality checks and method optimisation</div>

Table 4.5 Possible sources of error within this investigation

4.4.2 Quality control programme: Heavy metal extraction

Quality checks were conducted to assess both the reproducibility and efficiency of the two metal extraction techniques prior to initiation of the sampling programme. The checks were conducted using sub-samples from a test soil sample, a single large sample collected from the Town Moor, and a standard reference soil (SRS) (ORM Laboratory of the Government Chemist, ref no. GBW07406) of known metal concentration. The techniques were tested at the 95% level; 95%, or more, of the sub-samples were required to display Pb and Zn concentrations within $\pm 2s.d.$ of the overall mean

(Appendix 3). Quality assurance was maintained throughout the survey by the use of sample duplicates², replicates³, and blanks⁴. One test soil sample and one blank were included with each batch of samples extracted, enabling a quality check to be conducted.

4.5 SPATIAL PATTERNS, VARIATION AND SPATIAL DEPENDENCE

Problems regarding identification of the nature, extent and hazard of contaminated land stem from the often heterogeneous and random nature of anthropogenic contamination. At a site, different contaminants may have been deposited as a consequence of different and either single or multiple activities, making the prediction of their distribution and location problematic (Ross, 1994). This raises problems regarding the identification of contamination and the use of appropriate sampling strategies to reduce the risk of samples being non-representative of the contamination present at a site (Kofi Astane-Duah, 1996).

Constraints of time and money dictate that potentially contaminated sites must be assessed using sampling techniques, full site assessment being wholly impractical. Site survey involves a balance between resources and the need to generate the highest probability of locating contaminated areas. To maintain this balance sites are frequently sampled on a relatively coarse spatial scale, with areas suspected of being contaminated examined at a finer spatial scale. Hence sampling may be concentrated on areas displaying higher or problematic degrees of contamination (Kofi Astane-Duah, 1996). However, sampling determines that detail is lost in addition to incorporating the risk of failing to locate a contaminated hotspot or fully identify the extent of a problem, if it were to exist. Sampling tends however to be conducted with some degree of prior knowledge, gained either from an historical survey or site visits.

By definition, geographical data are inherently spatial in nature (Environmental Modelling: Spatial Dependence, no date). Hence analysing data, using classical

² duplicate – two sub-samples taken from the same sample and extracted with the same batch.

³ replicate – sub-samples from a batch are extracted more than once.

⁴ blanks – an extraction conducted with no soil in the vessel, just the reagents.

statistical tools that make no use of spatial information is often inappropriate (Isaaks and Srivastava, 1989). A growing body of tools, known as geostatistics, aimed specifically at exploring spatial information, has been utilised by the field of earth sciences for a number of years. These techniques, originally developed within the mining industry to evaluate ore deposits, offer a way of describing spatial structure and continuity. Geostatistical techniques, that examine relationships between sample points, allow sampling frequencies to be optimised to a given tolerance level and the assessor to determine levels of contamination at non-sampled points, within the sampled area, with some degree of reliability. Hence, land may be managed effectively, risk minimised and unnecessary cost avoided. Essentially, geostatistical analysis is a two step procedure: 1) the calculation and fitting of a model to an experimental variogram, which describes the spatial relationship between data points, and 2) the kriging process, which uses variogram parameters to enable accurate prediction and in turn interpolation.

4.5.1 Spatial patterns and variation

Relative frequency distributions and summary statistics, including measures of location, spread and shape, were used to determine the degree of within site soil Pb and Zn variation. As the aim was to examine variation in soil metal concentration raw data were used, including all outlying values. Frequency distributions provided a visual overview of site concentrations, whilst summary statistics provided information regarding the variability of the concentrations and symmetry of the distributions. Geochemical data sets are characterised by positive skewness exhibiting large numbers of low values and a few high or outlying values (Isaaks and Srivastava, 1989). This characteristic exerts substantial influence on statistics and as a consequence care must be taken in interpretation, particularly of measures of central tendency (Swan and Sandilands, 1995). A positively skewed data set exhibits a higher mean than median, the mean value being affected by the outliers.

Graduated symbol and colour pixel maps, produced using ArcView (ESRI), supplied an instant visual impression of soil heavy metal concentrations at the sites. Pixel maps presented a more easily interpretable picture of spatial distribution in the smaller plots. The maps provided information regarding:

- the location of high / low concentrations

- the proportion of each site displaying high / low concentrations
- the differences between concentrations of neighbouring samples
- associations between the concentrations of Pb and Zn

4.5.2 Geostatistical techniques

Variogram analysis and kriging were used to assess the spatial dependence / continuity of heavy metal concentrations within the soil of plots I, II and III. An accurate interpolation could only be determined for plot III ($0.5 \times 0.5\text{m}$ sampling frequency) as fluctuating variograms, with large nugget variances and unclear structures were seen for plots I and II. Appendices 5 and 6 outline the theory behind spatial dependence, determined via variogram analysis, and kriging, used for surface interpolation.

4.5.2.1 Exploratory Data Analysis

Geostatistical theory determines that data sets must meet a number of assumptions if variogram analysis is to be accurate, stationarity being the main condition that must be satisfied (Appendix 5). Over the years, different levels of stationarity have been defined, with the definition becoming increasingly less strict. Originally stationarity was defined according to the intrinsic hypothesis which constitutes two assumptions. Firstly, the expected value of a variable is constant and does not depend on position, hence the expected value is equal to the mean, and secondly, the expected squared difference between values at points a given distance apart is finite depending only on distance not on position. However more recently, the condition of quasi-stationarity has been adhered to. Quasi-stationarity assumes that properties remain stationary within smaller neighbourhoods, taking into account that properties may vary from one part of a large area to another (Webster and Oliver, 1990). The condition of quasi-stationarity has been adhered to during this investigation hence the local means and standard deviations must remain approximately constant across the sampled area. The less a data set is skewed and affected by outliers, the more likely it is to satisfy this condition (Kaluzny *et al.*, 1998).

Exploratory data analysis (EDA) was used (1) to examine the data for outliers that should be considered for removal prior to analysis and (2) assess the level of skewness to determine whether transformation was required to improve normality. In addition,

the data sets were examined to determine whether they met the condition of quasi-stationarity. MINITAB and Mathsoft's S-Plus with the spatial statistics module were used for this exploratory analysis.

Step one of the EDA consisted of a graphical examination of the data sets using both boxplots and stem and leaf diagrams in order to identify potential outliers within the raw data. Examples of these plots are shown within Figure 4.6. The boxplots exhibiting the mean and interquartile range of the data sets provide an indication of the distribution of the data points within the range, in addition to identifying outlying values. Stem and leaf diagrams play a similar role although data are arranged as a sideways histogram from which the actual data values can be read directly. Again this technique highlighted outliers. Those samples identified as exhibiting outlying concentrations were removed from the data sets before analysis proceeded.

It has been noted that a non-normally distributed data set may have a proportional effect on its variogram, causing distortion, increased sill and nugget variances, and fluctuating variogram values that conceal the real structure (Zhang and Selinus, 1997). Therefore following outlier removal the data were tested for skewness and transformed to normality where necessary. Data sets exhibiting a skewness coefficient $>|1|$ were considered to require transformation (Oliver personal communication). Many data sets exhibited a degree of positive skewness as is typical of soil pollution concentrations hence normality was improved by simple \log_{10} transformations.

The second step of EDA involved examination of the data to determine that the assumption of local stationarity had not been violated. This step involved the use of box-and-whisker plots, calculated for each row and column, to indicate whether samples were atypical to their neighbours. The technique is similar to that suggested by Cressie (1991) who plotted mean and median values across the rows and columns of gridded data. Figure 4.7 shows an example of a box-and-whisker plot displaying outliers for each row and column of the data set. Outliers identified by both row and column plots were removed from the data sets as these samples were considered to be violations of local stationarity. The box-and-whisker plots were also used to determine that no trends existed across the plots, for example, increases / decreases in the mean along either the rows or columns of the data. No trends were evident within the data sets examined.

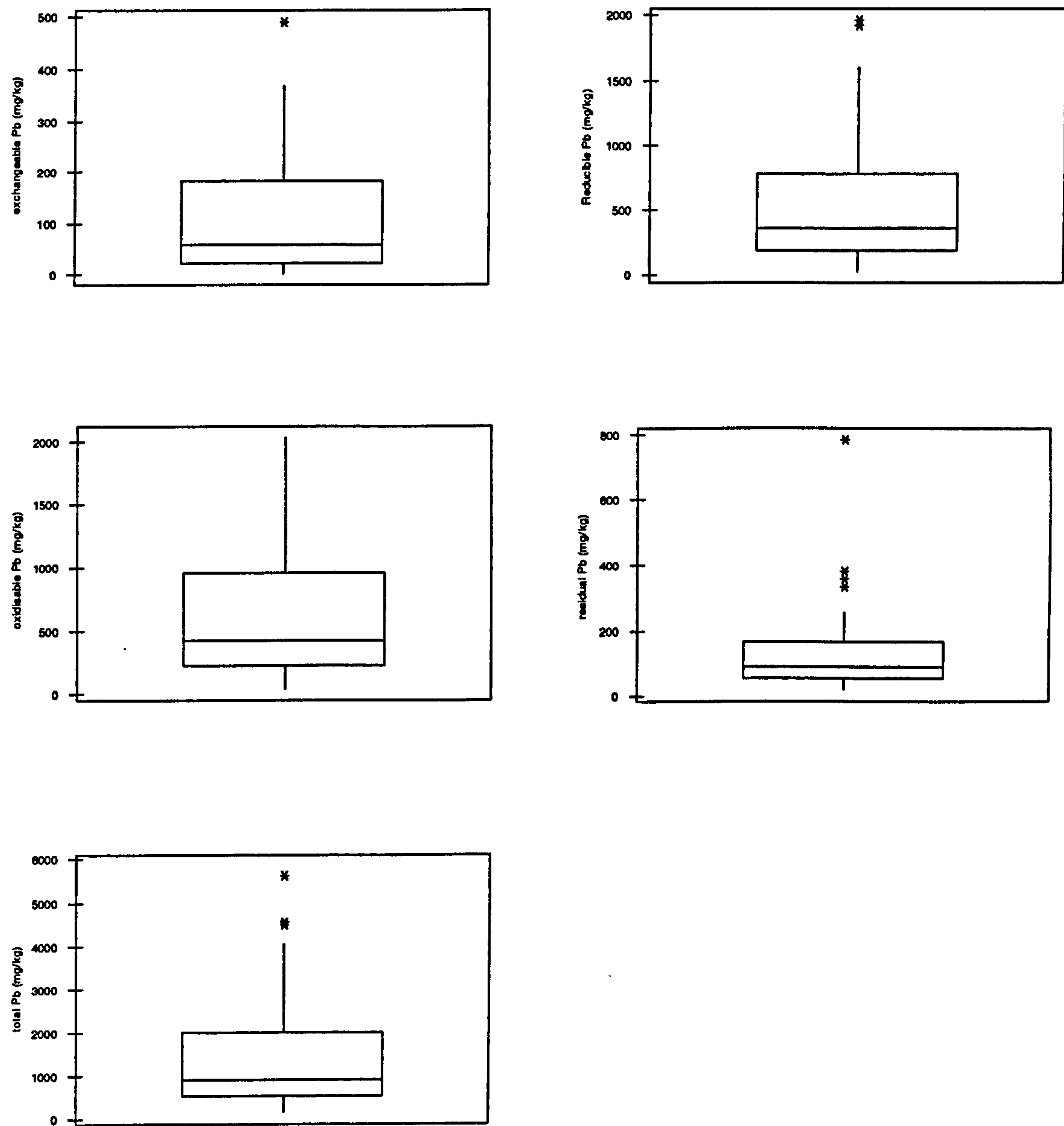


Figure 4.6 Box plots highlighting outliers (*), plot 1 top soil Pb data

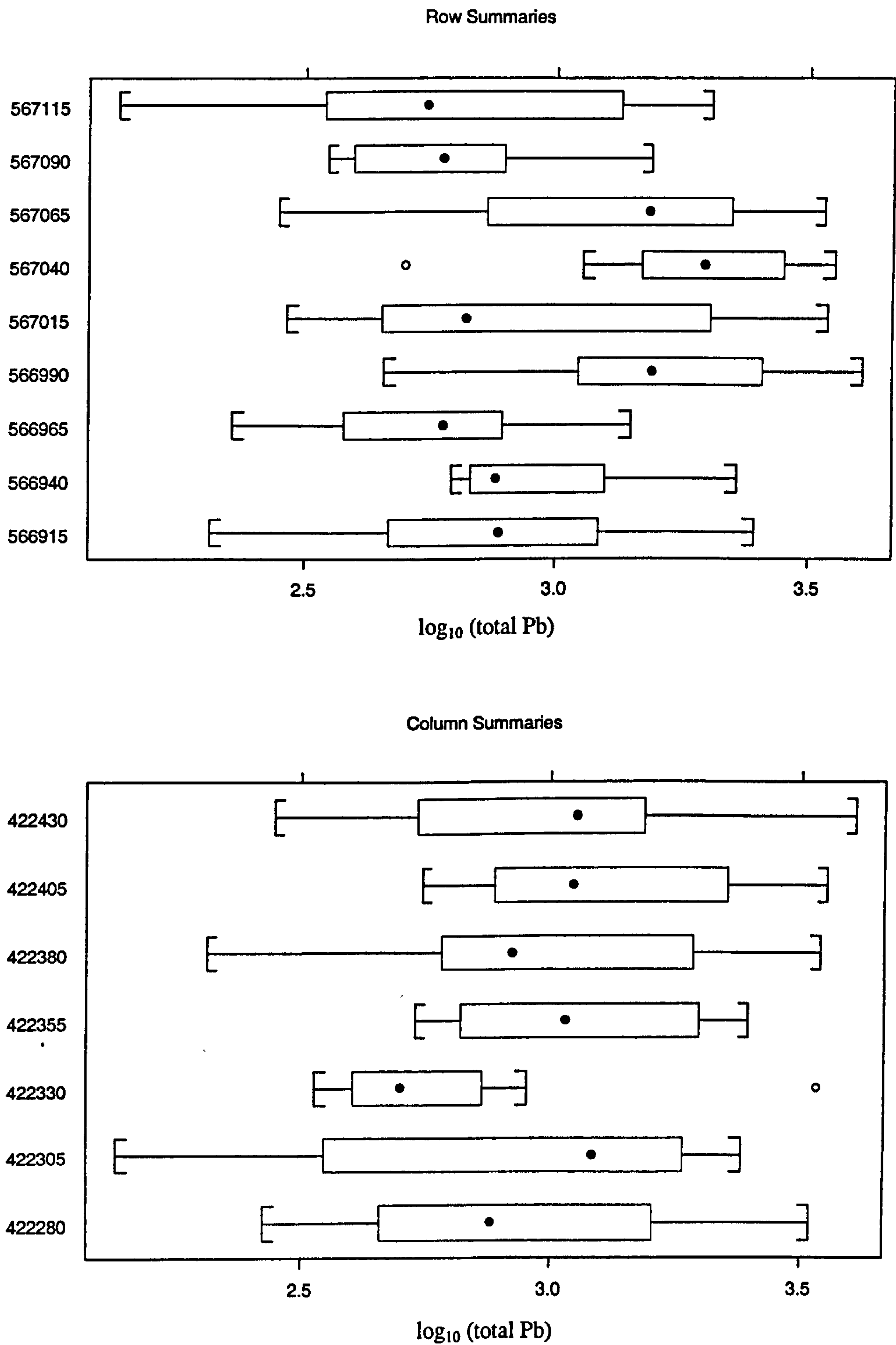


Figure 4.7 Box and whisker plots, highlighting possible deviations to the condition of quasi-stationarity, top soil total Pb (open circle represents potential outliers)

4.5.2.2 Variogram analysis and surface interpolation

Formation of an omni-directional variogram, a single variogram defining variation in all directions, is the first step in geostatistical analysis. This variogram includes more sample pairs than any directional variogram and is therefore more likely to show a clearer structure. Calculation of this variogram does not imply that spatial continuity is the same in all directions, but as direction plays no role, is useful in the determination of a number of parameters that may greatly affect structure. Parameters requiring optimisation are listed below:

- maximum distance of reliability / minimum number of pairs
- lag spacing / distance
- lag tolerance
- angular tolerance

Where parameters are not specified computation packages tend to choose default settings, many of which will define a reasonably clear structure. Care must be taken, however, as assuming that the default settings are the most appropriate can lead to a less well-defined variogram. The most important section of the variogram is the smaller lags as the kriging system is generally applied to the 16 or 25 nearest neighbours around the point estimated (Delcourt *et al.*, 1996). Variogram analysis was conducted using the statistical package S-Plus with the add on spatial statistics module.

Maximum distance of reliability / minimum number of pairs

The maximum distance of reliability or the maximum distance over which a variogram may be calculated (h) was defined by Journel and Huijbregts (1978) as less than the maximum distance over which samples had been collected (D) divided by two ($h < D/2$). A rule which, in addition to the least number of pairs, 30, for which a semi-variance may be accurately calculated, also defined by Journel and Huijbregts (1978), is still used today by many geostatisticians. These rules have been abided for this study, although it has been noted that Oliver and Webster (1991), for example, also define other criteria. These authors stated that a minimum of 100 and probably nearer 200, samples should be used to estimate an isotropic variogram with reasonable precision, and that where a variogram is anisotropic even more data are required. In general these rules have not been adhered to. Kuzel *et al.* (1993), for example, produced anisotropic

variograms from 121 samples when investigating the spatial variability of cadmium in soil, whereas Paz *et al.* (1996) used 53 samples, Boekhold and Van Der Zee (1992) 166 and Saldana *et al.* (1998) 49. This study calculates variograms for three plot sites, I, II and III, where 63, 64 and 121 samples have been collected, respectively. The author is aware of the accuracy problems that may be caused by this few samples, hence analysis has been limited (Section 5.3).

Lag spacing

The lag spacing / distance, the distance between successive h-scatter plots, can greatly affect the structure of a variogram, a smoother variogram being produced for larger lag spacing (Figure 4.8). The ideal lag spacing is determined by the calculation of omnidirectional variograms for a number of lags, using the default lag tolerance (half the lag spacing). Spacing must be chosen which produces a reasonably smooth variogram but does not conceal the real structure of the relationship. The grid spacing is usually a suitable lag if samples are located on a regular grid.

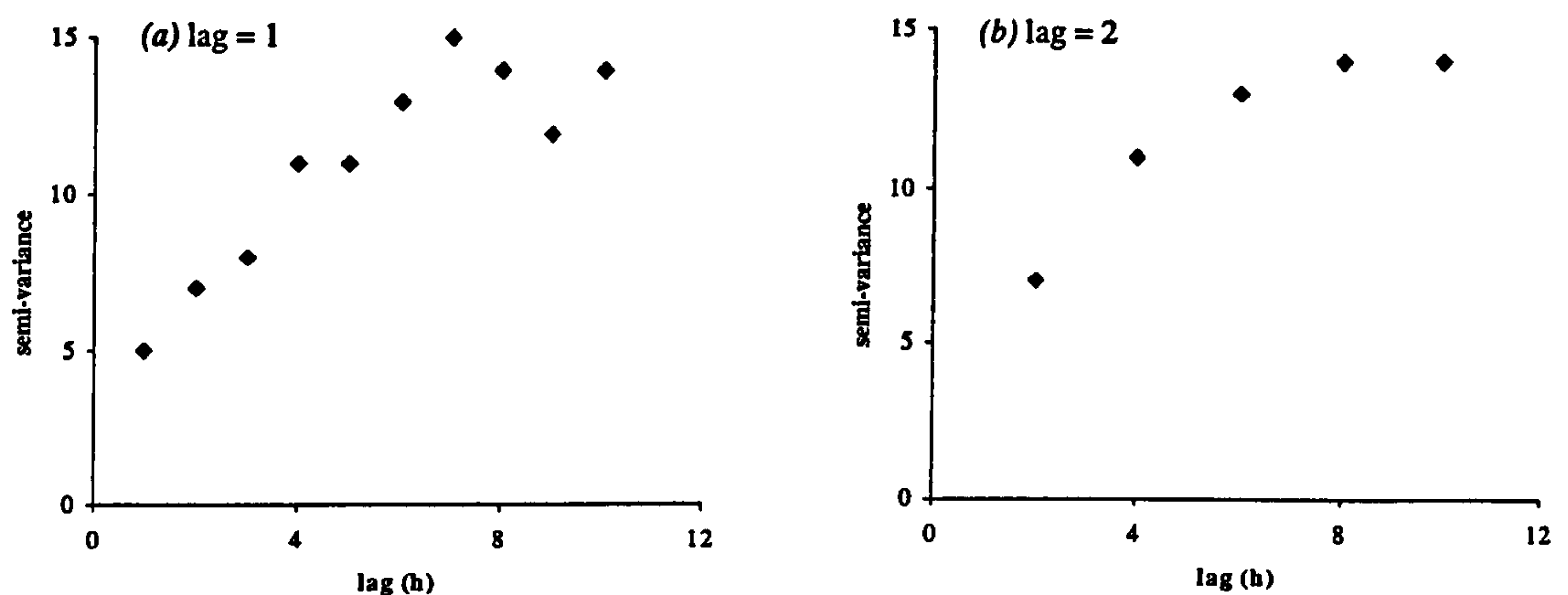


Figure 4.8 The effect of lag spacing on the variogram, (a) lag 1; (b) lag 2.

Lag tolerance

The lag tolerance, the tolerable distance allowable on the lag, is set by default as half the lag spacing, this being the most common choice for this parameter. However, when samples are located on a regular grid, smaller tolerances may be chosen. Choosing a smaller tolerance may make variogram structure clearer, but it can result in some pairs

not being included. Figure 4.9 defines lag tolerance. To determine the most appropriate tolerance, omni-directional variograms are produced for a number of different tolerances, the best being the one that produces the most well behaved variogram with the clearest structure.

If an omni-directional variogram of well-defined structure cannot be produced there is little point attempting to produce directional variograms. Directional variograms utilise fewer points and therefore are liable to be more erratic.

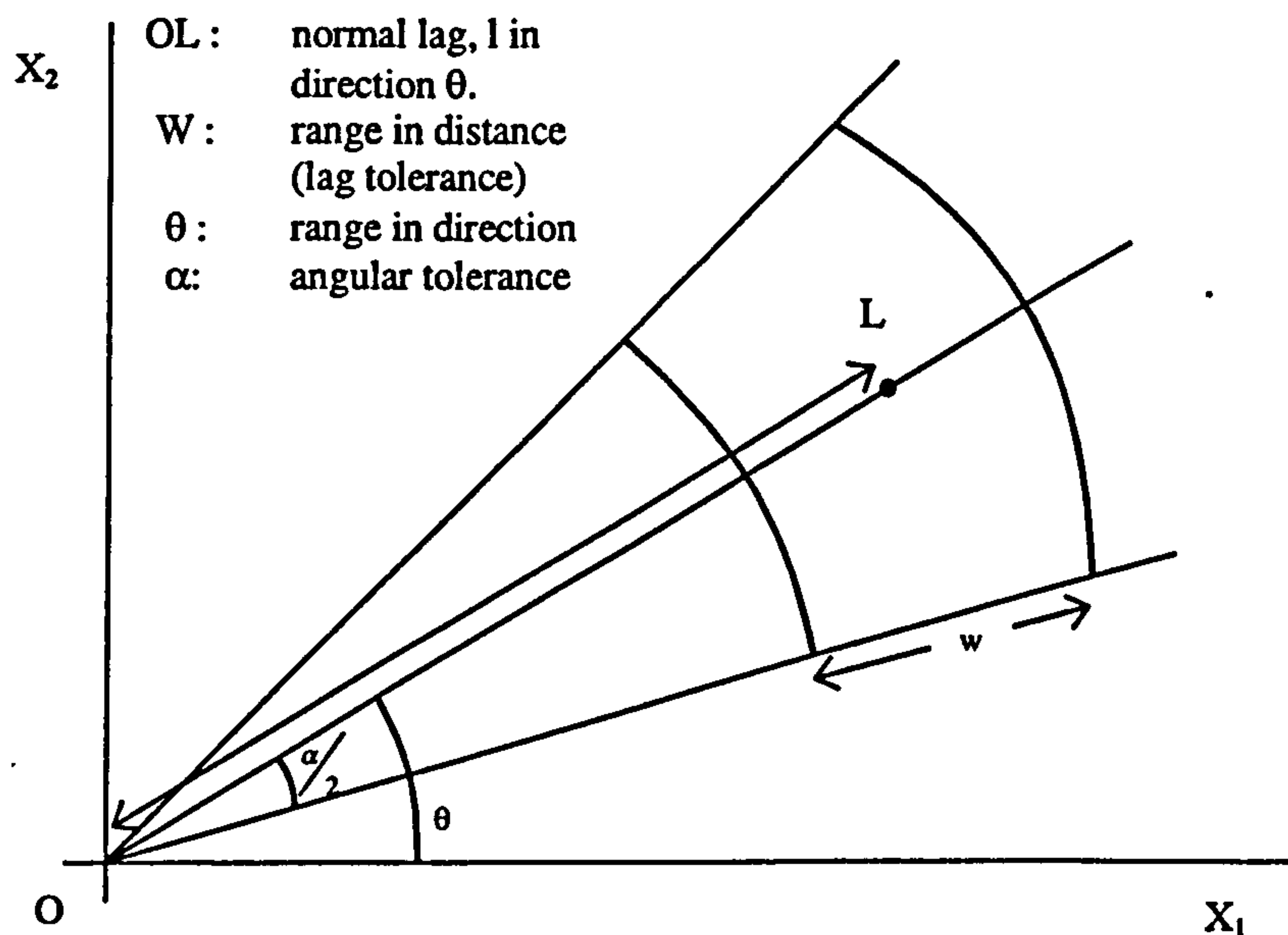


Figure 4.9 Lag and angular tolerance

Angular tolerance

Assuming sufficient data are available directional variograms may be produced, using the optimised parameters, once a well-behaved omni-directional variogram has been defined. The production of directional variograms allows the analyst to determine whether the property varies differently in different directions, i.e. whether it exhibits anisotropy. In order to determine anisotropy, variograms must be calculated for a minimum of three directions (Webster and Oliver, 1990), although the convention is to produce four variograms in the following directions, N-S, E-W, NE-SW, SE-NW (Variograms, no date).

An angular or directional tolerance (Figure 4.9) is often allowed when calculating directional variograms, particularly where data points are non-evenly scattered. Ideally, this tolerance should be as small as possible to limit blurring of the anisotropy, but too small a directional tolerance can provide too few points and hence an erratic variogram. Variograms should be produced for a minimum of four directions using a variety of angular tolerances. From these the smallest tolerance should be chosen so that the directional variograms are well defined, but still displaying anisotropies.

Variogram models

The variogram model defining the relationship between points on the optimised experimental variogram⁵ is described by a minimum of three parameters and fitted to the experimental variogram using a least squares regression. The model or theoretical variogram⁶ is a function describing the relationship i.e. spatial dependence, between sample points of the experimental variogram. Appendix 5 outlines the main types of variogram model. The model parameters may be used to predict, using the method of kriging, values at non-sampled areas producing an accurate surface interpolation (Appendix 6).

Surface interpolation

Omni-directional variogram parameters were used to produce 3D surface interpolations for plot III, using the method of ordinary (punctual) kriging (Appendix 6), the best method for estimating the concentration of pollutants within soil (Oliver and Webster, 1991). Using S-Plus, kriging matrices were determined and kriging predictions and standard errors computed for non-sampled locations. Predictions were generated for a number of grids, these included 20×20 , 30×30 , 40×40 and 50×50 nodes, 40×40 being the default set by the package. Standard errors were compared to determine the best prediction grid. The 3D interpolations of the predictor surface and standard errors were examined from the corners of the plot.

⁵ experimental variogram – the variogram calculated from data upon which a variogram model is fitted i.e. the average squared difference between measured values as a function of the distance separating measurements.

⁶ theoretical variogram – a function fitted to the experimental variogram.

4.6 FRACTIONATION AND BEHAVIOUR

Heavy metals are input into the environment from a wide variety of sources, both natural and anthropogenic, with single sources often emitting several different forms of a metal (Ross, 1994). Soils have the tendency to act as a sink for heavy metals, however the chemical forms and their stability, in addition to environmental conditions determine how mobile or toxic a metal may be. Research has shown soil heavy metal retention and hence mobility, bioavailability and potential toxicity to be heavily influenced by edaphic conditions (Ross, 1994; Hooda and Alloway, 1998; Rieuwerts *et al.*, 1998).

Within the soil, metals are not decomposed but remain as ions, although speciation may change if soil conditions change. For example, a change in pH, resulting in increased acidity has on the whole been found to increase availability and mobility of metals within the soil. Organic matter on the other hand, provides binding sites for heavy metal ions, increasing soil retention (Section 2.6). Despite this, the degradation of organic matter may lead to the release of metals into the soil system.

The soil is subject to both short-term fluctuations and gradual alterations in response to changes in management and environmental factors, with practices such as liming and fertiliser application known to alter edaphic conditions. Hence, the affects of changing soil conditions must be considered when deciding on the management strategies for heavy metal polluted soils (Alloway, 1995; Kofi Asante-Duah, 1996). Not only can altering the fractionation of metals have potentially disastrous affects on human health but also on plants, soil ecological communities and possibly ground water quality.

Sequential extraction methods, designed to extract metals from soil according to their relative availability, are useful tools in developing an understanding of the complex nature of heavy metal reactivity and binding forms within soil (Barona and Romero, 1996). These techniques provide valuable information regarding fractionation and hence potential bioavailability and mobility of heavy metals (Section 2.5). Information regarding the partitioning of heavy metals and the relationships between the fractions and soil properties provides an insight into the behaviour and fate of heavy metals

within the system. Despite potential hazard, common legislative guidelines have yet to specify values for different metallic forms (Section 2.7).

4.6.1 Fractionation

Relative frequency distributions, summary statistics and spatial plots of the raw data were used to determine the concentration variation and spatial distribution of the four Pb and Zn fractions within the soil of plot I (Section 4.5.1). Percentages were used to determine the partitioning of the metals between the fractions and top soil / sub soil enrichment ratios calculated to examine redistribution within the soil. The χ^2 test determined the significance of observed differences in the heavy metal partitioning between the top and sub soil. Variograms were also computed allowing the spatial continuity of the various fractions to be examined and compared.

4.6.2 Behaviour

4.6.2.1 Correlation and Regression

Certain soil properties have been seen to influence the fate of heavy metals within the soil system, affecting the retention, immobilisation capacity and hence bioavailability and mobility (McKenzie, 1980; King, 1988; Ross, 1994; Alloway, 1995; Hooda and Alloway, 1998) (Section 2.6). Many studies have found associations between heavy metals and soil properties using the techniques of correlation and regression. Correlation is a measure of the strength and direction of the relationship between the two variables, for example, exchangeable Pb concentration and pH. Regression analysis on the other hand, enables the form of the relationship to be established and for the value of one variable to be predicted from the pattern of another. The level of explanation is also calculated (Appendix 7).

Correlation and regression analyses were used to examine associations between Pb, Zn and soil properties at plot I following the removal of outlying data. Correlation implies a statistical relationship between two sets of variables rather than causation and is used to confirm / refute a scientific hypothesis. Correlation does not imply that a hypothesis is true but indicates the probability that the results would have been obtained by chance given the model. A Null hypothesis, H_0 , of no association between two variables x and y , is accepted unless correlation coefficients exceed the 95% ($p < 0.05$) critical value for

the given degrees of freedom (d.f. = $n-2$). If critical values are exceeded an alternative hypothesis, H_1 , of an association between variables x and y is accepted. H_1 is not accepted with 100% certainty as H_0 can be wrongly rejected.

Following the removal of outliers, the data set varied in size from $n = 52$ (d.f.=50) to $n=63$ (d.f.=61), hence a number of critical values were required to assess associations (Table 7.2). The reasonably large size of the data set determined that the critical values for the rejection of H_0 were relatively low, hence scatter graphs exhibiting a high degree of scatter were often found to display significant associations exceeding critical values, leading to the rejection of H_0 . The strength of an association, for which many conventions exist, can however be more informative. For the purposes of this investigation, a correlation exhibiting a coefficient of $< |0.45|$ is classed as weak, whilst a coefficient between $|0.45|$ and $|0.75|$ is classed as moderate and $>|0.75|$ as strong (Oliver, personnel communication). Regression analysis determined the form of any relationships, with R^2 values used to indicate the level of explanation between properties.

4.6.2.2 *Principal Components Analysis (PCA)*

Correlation between soil properties has led many soil scientists to use multivariate techniques in an attempt to extract the most meaningful variables, or a combination of them, from large data sets that may be difficult to interpret (Berg *et al.*, 1994; Theocharopoulos *et al.*, 1997). Barona and Romero (1996) used principal component analysis to study the relationships between the concentration of metals accumulated in soil fractions, determined using sequential extractions, and a number of soil properties thought to affect speciation. They observed clustering of variables into groups, the groups containing variables that were highly correlated with one another. The technique enabled redundant variables to be eliminated. (Appendix 8).

Correlation-based PCA was used to investigate the relationships between the Pb and Zn fractions, determined via sequential extraction, and certain soil properties thought to affect heavy metal retention within the soil. Correlation-based PCA is appropriate for use with environmental variables as the technique uses standardised data to produce axes with comparable, dimensionless scales. Standardisation is essential for this type of data as it often consists of a variety of measurement scales that may distort results.

Where PC1 and PC2 explain < 50% of the total variance, two component PCA ordination can give an inadequate and potentially misleading picture, more axes must therefore be included. As a general rule, a picture that accounts for 70-75% of the original variation is likely to explain the structure well (Clarke and Warwick, 1994). The theory and assumptions behind PCA are outlined in Appendix 8.

4.6.2.3 Non-hierarchical cluster analysis

Due to complexity many data sets are difficult to interpret, hence multivariate methods of classification can be used to provide a simpler picture that is easier to comprehend. Classification enables individuals to be discussed in terms of one or more groups using names rather than lists of characteristics. Two main types of classification exist within soil survey literature, these being hierarchical and non-hierarchical. Hierarchical methods have tended to dominate, however non-hierarchical methods are often more appropriate where populations lack any inherent structure (Webster and Oliver, 1990).

Non-hierarchical cluster analysis was performed using Genstat (Genstat 5 Committee, 1987) following the procedure outlined in Webster and Oliver (1990) and Chappell *et al.*, (1998). Initially all 26 variables and 63 sites were included in the analysis, including those previously shown to be outliers. The test criterion SS_w was chosen for optimisation of the classification, this criterion being the most appropriate for weakly clustered data (Appendix 9). Previous examination of the PCA eigenscores in the plane PC1 and PC2 indicated that data were poorly clustered, if at all. SS_w is a measure of compactness or dispersion within groups being the sum of squares of deviation from the cluster means. Prior to analysis, data were standardised to zero mean and unit variance, a pre-requisite of the SS_w criterion.

Initially samples were divided into 10 to 20 evenly sized groups on the basis of order within the spreadsheet (Appendix 9), more groups being chosen than were expected to exist. The transfers and swaps algorithms within Genstat were then used to determine an optimum classification based on the test criterion. Due to the weak clustering of the data, this is expected to be a local rather than a global optimum. Wilks's criterion L was used to determine the optimal number of classes for the cluster analysis via the plotting of g^2L vs. g , where g = number of classes. An optimum is reached where the graph exhibits a trough (Appendix 9). Hence the final analysis was optimised for both

number of classes and compactness of groups (SSw). The classification was examined as a pixel map of spatial distribution.

Due to the non-clustered nature of the data several optimum classifications existed for all 26 variables. In addition, the optimum number of groups was high giving the impression that the data were possibly random. Further classifications were therefore conducted using smaller numbers of selected variables allowing plot I to be classified according to top, sub soil and combined layer Pb and Zn fractionation.

CHAPTER 5

SPATIAL PATTERNS, VARIATION AND DEPENDENCE

Summary

This chapter investigates the spatial patterns, variation and dependence of the metals Pb and Zn within the soil of open public access areas in north-central Newcastle. The chapter has been divided into 5 main sections that focus down to an increasingly fine sampling scale. Section 5.1, the introduction, provides an overview of the analyses conducted. Section 5.2 describes the variation in soil total Pb and Zn concentrations at four sites and three plot sites. Section 5.3 investigates the spatial dependence / continuity between sample points at the three plots, whilst section 5.4 utilises the results of section 5.3 to produce a surface interpolation of soil total Zn concentrations in plot III, the most intensively sampled area. Section 5.5 summaries the chapter, reiterating the main findings and identifying areas for discussion in chapter 8.

5.1 INTRODUCTION

This chapter describes within site soil Pb and Zn concentration and spatial variation from the site (140ha) to the plot scale (25m²) utilising increasingly finer sampling scales (Section 5.2). A multi-stage sampling technique has been employed where information from initial site surveys was used to identify a plot area (200 × 150m) for further more detailed investigations at finer sampling scales (25 × 25m, 5 × 5m and 0.5 × 0.5m) (Section 4.2). Within the plot, smaller areas were isolated and the frequency of sampling increased until the degree of spatial dependence / continuity could be determined using geostatistical techniques (Section 5.3). Once clearly structured variograms had been produced sampling frequency was no longer increased (Appendix 5). The final step was the determination of an appropriate variogram model, the use of kriging to produce surface interpolations (Section 5.4), and hence, the estimation of soils Pb and Zn concentrations within non-sampled areas.

5.2 SPATIAL PATTERNS AND VARIATION

This section describes within site / plot soil Pb and Zn concentrations and spatial variation at a number of sites and sampling scales. The data are presented from the largest ($200 \times 200\text{m}$) to the smallest ($0.5 \times 0.5\text{m}$) scale, so as to provide the reader with an insight into scales of variation. Means, medians standard deviations, ranges and measures of skewness have been used in conjunction with frequency plots to assess the extent and nature of the contamination. Spatial variation is determined from concentration plots (Section 4.5.1). Levels of contamination and potential hazard are assessed via the application of current British and Dutch legislative guidelines, in addition to the HPTULT¹ values calculated by Aspinall *et al.* (1988) using the method described by Davies (1983) (Appendix 1).

5.2.1 $200 \times 200\text{m}$ scale

The study of Mellor and Bevan (1999) conducted at a $200 \times 200\text{m}$ scale identified a wide range of topsoil Pb concentrations at the four sites chosen for this investigation. Contamination at these sites (the Town Moor, Nuns Moor, Hazelrigg nature reserve, and S. Gosforth (Figure 5.1) ranged from $< 79.9\text{mg/kg}$ to $> 2000\text{mg/kg}$. Top soil Zn concentrations were also investigated although have yet to be published. These authors collected 78 top soil samples from the four sites, 40 from the Town Moor, 27 from Nuns Moor, ten from the Hazelrigg nature reserve and one from the S. Gosforth site.

5.2.1.1 *Total Pb*

Despite the similar range, soil Pb concentrations were on the whole greater and displayed a higher degree of within site variation than soil Zn (Figure 5.2). The maximum Pb concentration was found at the S. Gosforth site, a 1ha green space located within a housing estate (Figure 5.2a). The one sample collected from this site displayed a Pb concentration nearly three times the British ICRCL guideline for public access areas, 2000mg/kg . The authors determined that soil Pb concentrations on the Town and Nuns Moors, two areas of old common land now enclosed by urban development, consistently exceeded the HPTULT value, 80mg/kg . A number of samples exceeded the Dutch action value, 530mg/kg (Appendix 1); these were scattered across Nuns

¹ HPTULT – Highest Probable Threshold for Uncontaminated Land in Tyneside.

Moor, mainly in the vicinity of Newcastle Golf Course, although the north west corner of Nuns Moor exhibited the highest concentration (Figure 5.2a). Soil of the Hazelrigg nature reserve, a reclaimed spoil tip located on the northern boundary of the Ouseburn catchment, exhibited relatively low concentrations of total Pb, the highest Pb concentrations being found near the centre and towards the eastern edge of the site (Figure 5.2a). Concentrations did not exceed the ICRL guideline, although one sample exceeded the Dutch action value and three the HPTULT value. At all four sites, soil Pb contamination appeared to be localised or hot-spot in nature, with samples containing high concentrations often isolated and surrounded by samples with relatively low concentrations.

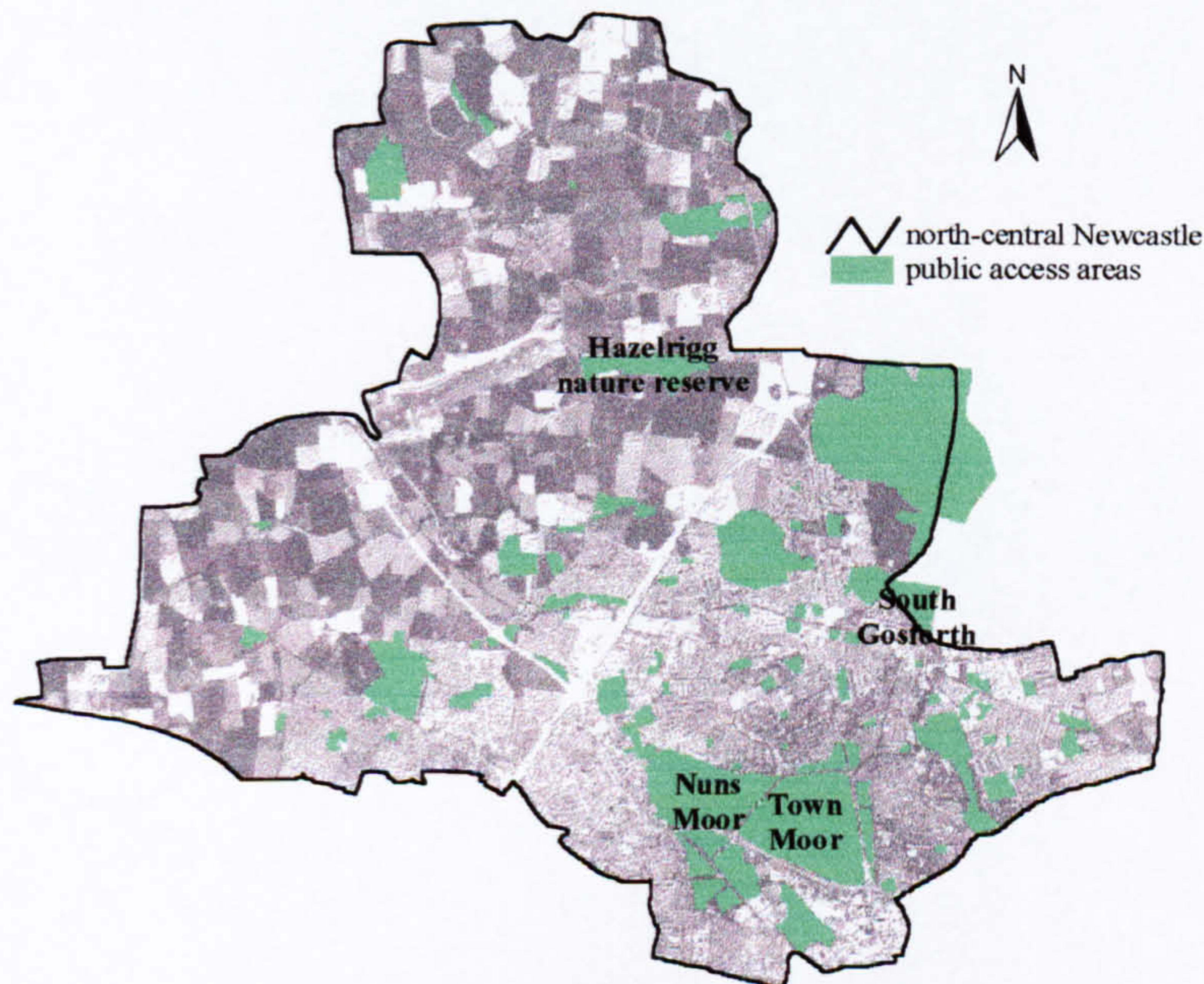


Figure 5.1 Location of chosen sampling sites within north-central Newcastle

5.2.1.2 Total Zn

Mellor and Bevan (unpublished) also identified a large range in top soil Zn concentration although, they determined that there was little spatial variation. Again the S. Gosforth site exhibited highest Zn concentration, the soils of the Town Moor, Nuns Moor and the Hazelrigg nature reserve exhibiting notably lower concentrations (Figure 5.2b). A British ICRL guideline has not been specified for Zn within the soils of open parkland although all concentrations, except that at the S. Gosforth site, fell below the

Dutch action level of 720mg/kg. Four samples exceeded the HPTULT value, 345mg/kg, one from each site (Appendix 1). Again spatial variation appeared to be hot spot in nature.

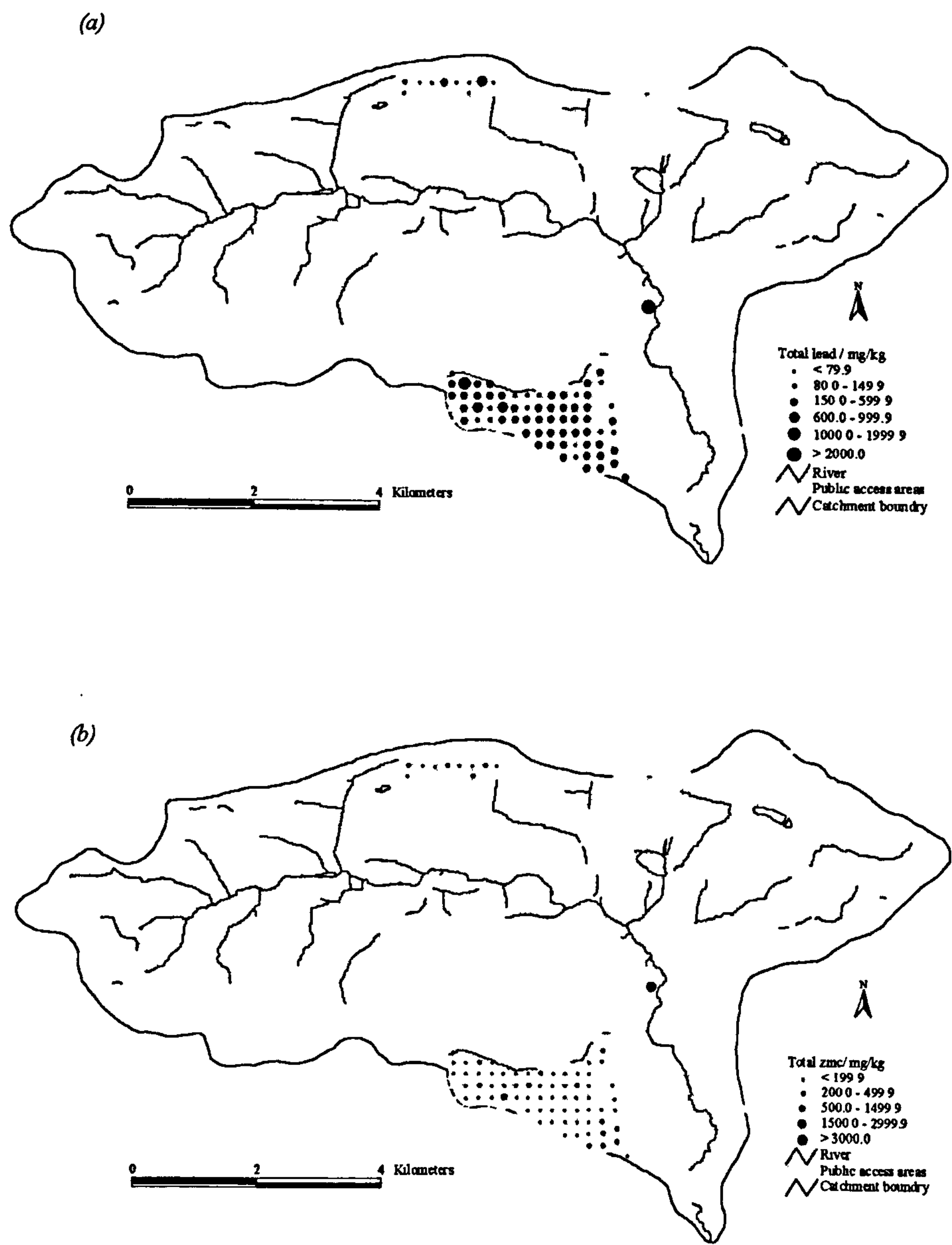


Figure 5.2 Top soil heavy metal concentration at chosen sites Ouseburn catchment (a) total Pb, (b) total Zn. Adapted from Mellor and Bevan (1999)

5.2.2 Site scale: 100 × 100m to 15 × 15m

Areas within the sites described in Section 5.2.1 were sampled on a finer scale to enable more detailed information regarding spatial patterns and variation to be gathered. The areas were sampled on a variety of scales with a different number of samples collected from each area. Sampling frequencies ranged from 100 × 100m to 15 × 15m (Table 5.1). In general the concentrations of top soil Pb and Zn were similar to those identified by Mellor and Bevan (1999).

	Town Moor	Nuns Moor	Hazelrigg	S. Gosforth
sampling frequency (m)	100 × 100	100 × 100	50 × 50 50 × 100	15 × 15
no. of samples	32	21	50	35

Table 5.1 Site sampling frequencies

5.2.2.1 Total Pb

Soil total Pb concentrations varied dramatically between the four sites, with the S. Gosforth site exhibiting the greatest range. Similar mean concentrations were noted at the Town Moor and S. Gosforth sites, although the Nuns Moor site exhibited a notably higher and Hazelrigg nature reserve a lower average concentration. All four sites exhibited positively skewed frequency distributions (Table 5.2, Figure 5.3).

		Town Moor	Nuns Moor	Hazelrigg	S. Gosforth
Pb (mg/kg)	mean	363.8	675.8	111.0	396.9
	median	306.4	349.2	91.6	220.0
	s.d.	181.3	744.0	80.9	908.2
	max	815.6	2837.8	557.8	5598.0
	min	129.8	93.0	31.4	140.0
	skewness	1.3	1.8	3.8	5.9
Zn (mg/kg)	mean	118.6	81.9	105.0	194.4
	median	90.3	73.8	67.1	135.0
	s.d.	114.1	28.4	152.1	207.3
	max	712.0	158.6	1082.0	1328.0
	min	61.6	48.2	20.2	86.8
	skewness	4.9	1.4	5.7	5.1

Table 5.2 Site summary statistics

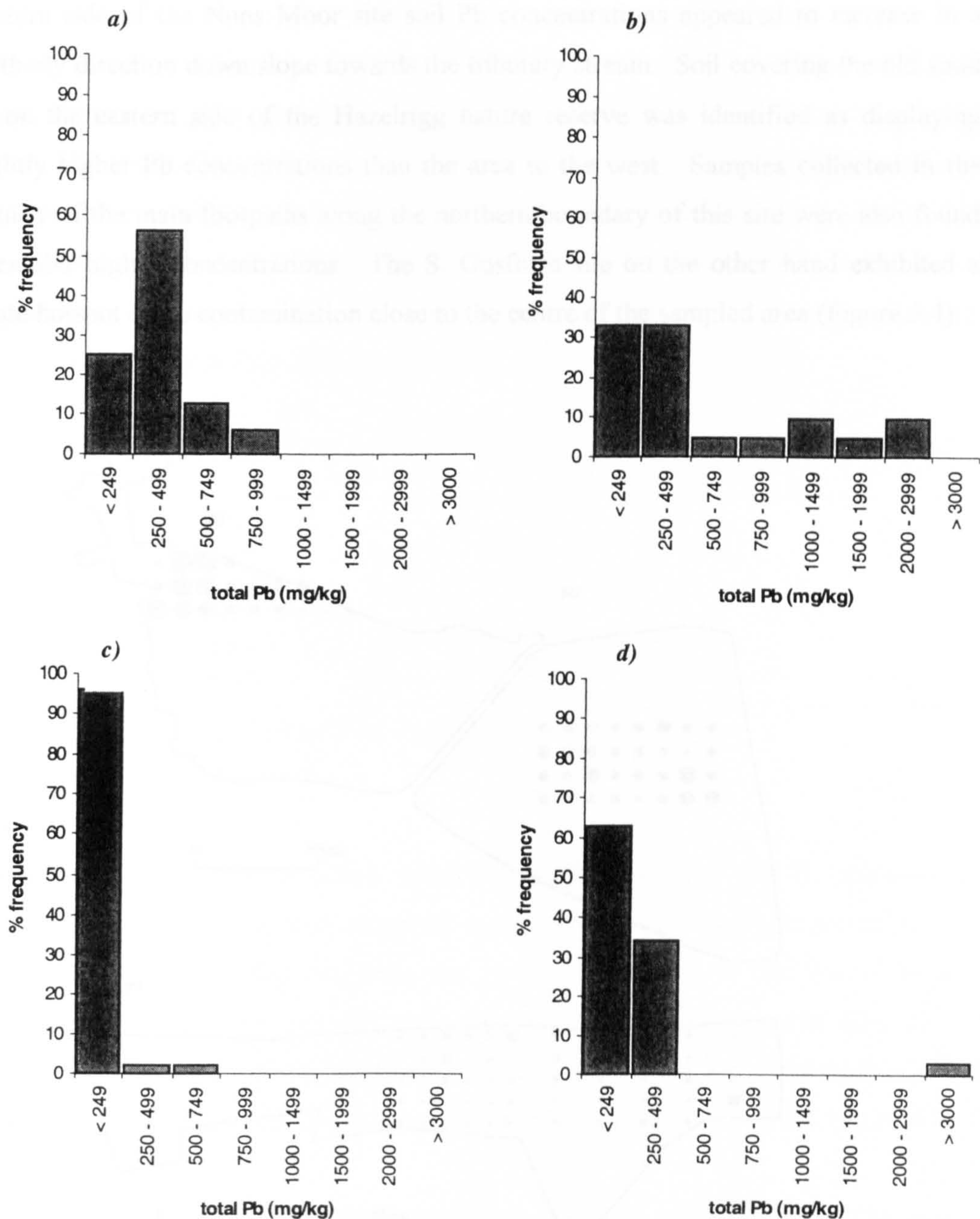


Figure 5.3 Site top soil total Pb concentrations, (a) Town Moor, (b) Nuns Moor, (c) Hazelrigg nature reserve, (d) S. Gosforth

In general, the contamination appeared to be localised and random in its spatial distribution, with isolated samples often exhibiting higher Pb concentrations. It was noted however that the south eastern corner and western side of the Town Moor and Nuns Moor sites, respectively, displayed consistently higher concentrations. On the

western side of the Nuns Moor site soil Pb concentrations appeared to increase in a northerly direction down slope towards the tributary stream. Soil covering the old spoil tip on the eastern side of the Hazelrigg nature reserve was identified as displaying slightly higher Pb concentrations than the area to the west. Samples collected in the vicinity of the main footpaths along the northern boundary of this site were also found to exhibit higher concentrations. The S. Gosforth site on the other hand exhibited a single hotspot of Pb contamination close to the centre of the sampled area (Figure 5.4).

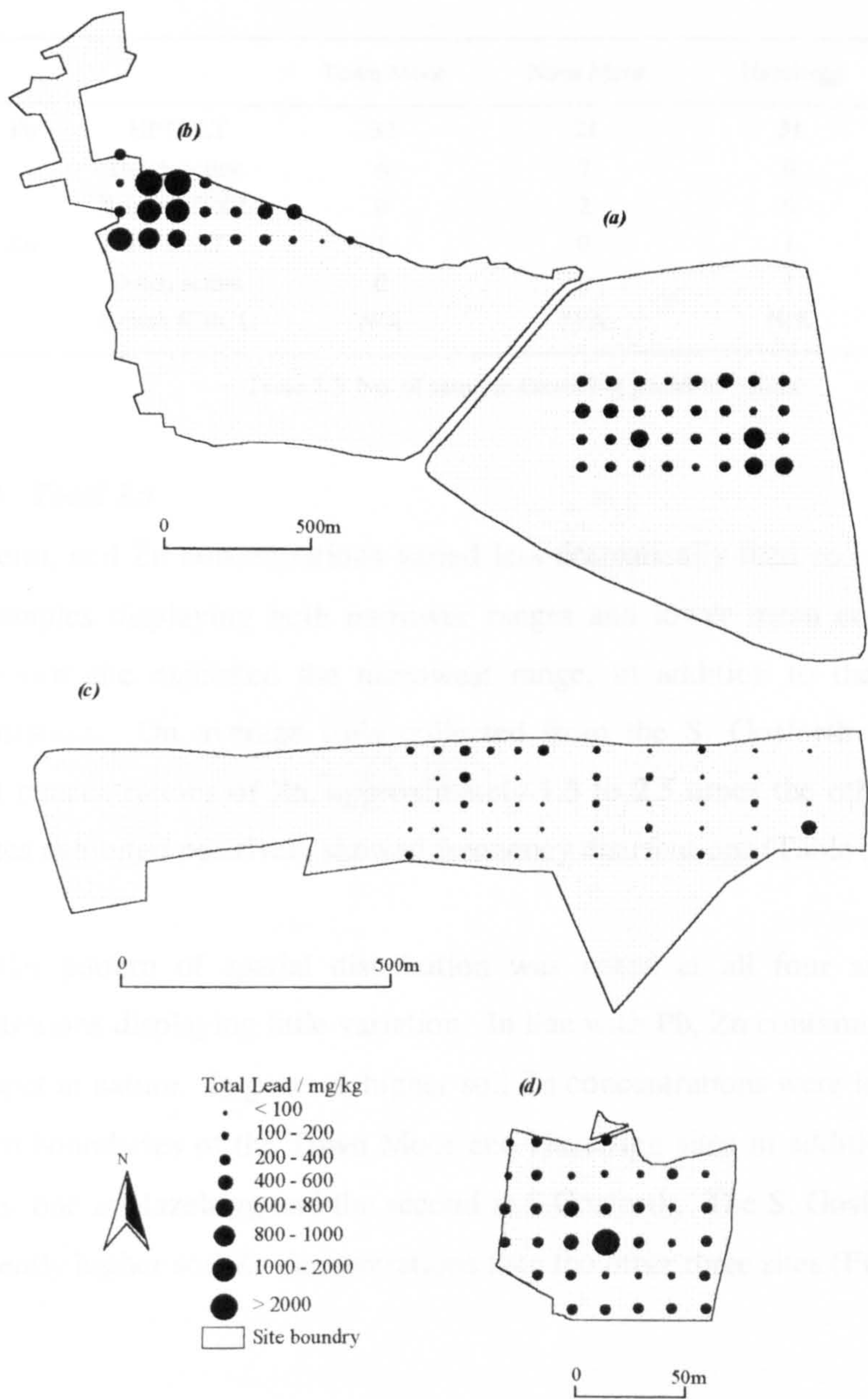


Figure 5.4 Site top soil total Pb concentration, (a) Town Moor; (b) Nuns Moor; (c) Hazelrigg nature reserve; (d) S. Gosforth

A number of samples collected from these four sites exceeded British ICRCL, Dutch action and HPTULT guideline values for soil Pb concentrations. The HPTULT value was exceeded by all samples collected from the Town Moor, Nuns Moor and S. Gosforth sites, although despite a number of samples exceeding the Dutch action guideline only three exceeded the ICRCL trigger concentration. These samples were collected from the Nuns Moor and S. Gosforth sites. Pb concentrations at the Hazelrigg nature reserve fell below both the British trigger and Dutch action guidelines although, a number of samples exceeded the HPTULT value (Table 5.3).

		Town Moor	Nuns Moor	Hazelrigg	S. Gosforth
Pb	HPTULT	32	21	31	35
	Dutch action	6	7	0	1
	British ICRCL	0	2	0	1
Zn	HPTULT	1	0	1	1
	Dutch action	0	0	1	1
	British ICRCL	N/A	N/A	N/A	N/A

Table 5.3 No. of samples exceeding guideline values

5.2.2.2 Total Zn

In general, soil Zn concentrations varied less dramatically than soil Pb concentrations, with samples displaying both narrower ranges and lower mean concentrations. The Nuns moor site exhibited the narrowest range, in addition to the lowest mean Zn concentration. On average soils collected from the S. Gosforth site contained the highest concentrations of Zn, approximately 1.5 to 2.5 times the other three sites. All four sites exhibited positively skewed frequency distributions (Table 5.2, Figure 5.5).

A similar pattern of spatial distribution was noted at all four sites, with soil Zn concentrations displaying little variation. In line with Pb, Zn contamination appeared to be hotspot in nature. In general, higher soil Zn concentrations were identified along the northern boundaries of the Town Moor and Hazelrigg sites in addition to two isolated samples, one at Hazelrigg and the second at S.Gosforth. The S. Gosforth site exhibited consistently higher soil Zn concentrations than the other three sites (Figure 5.6).

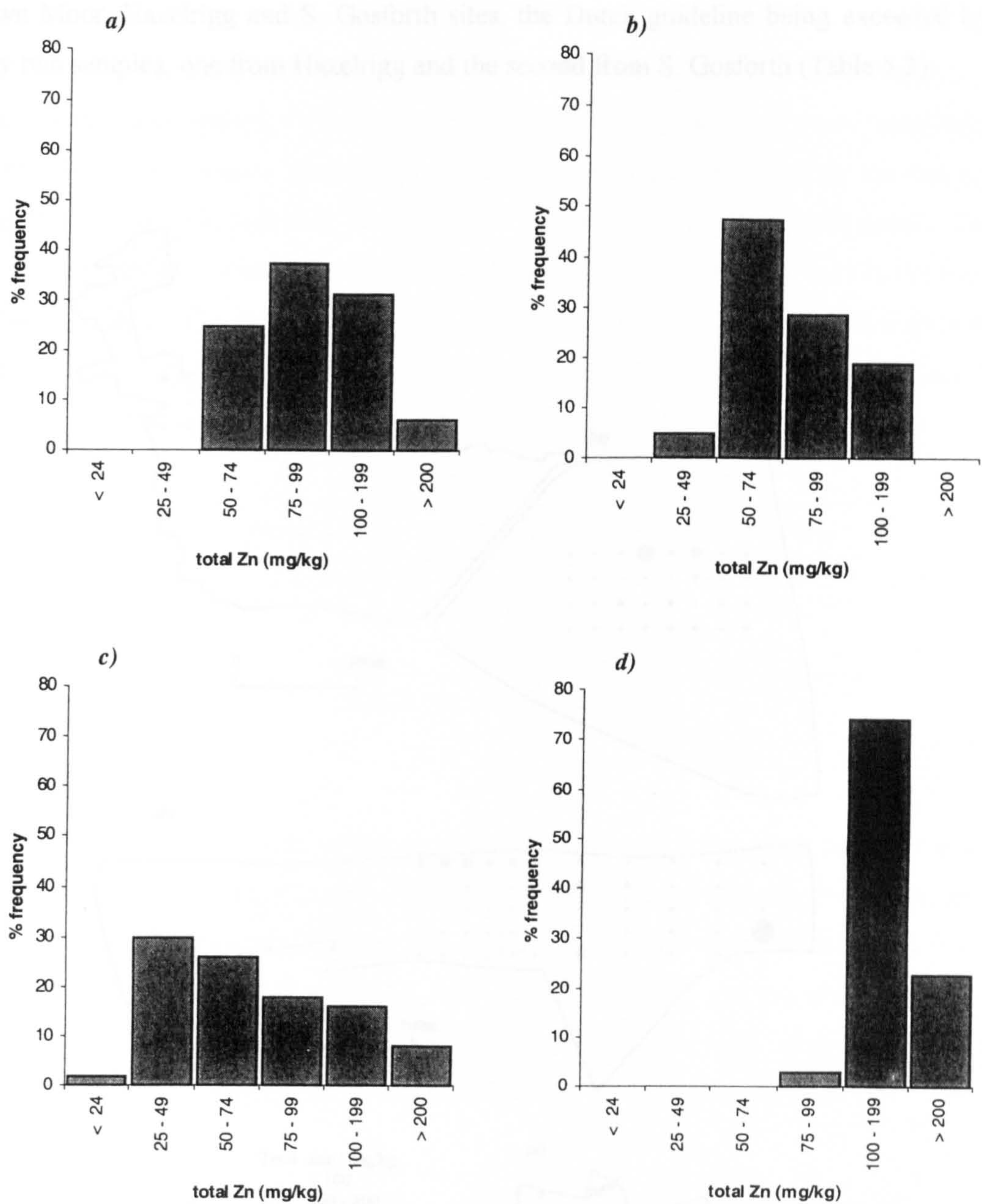


Figure 5.5 Site top soil total Pb concentrations, (a) Town Moor, (b) Nuns Moor, (c) Hazelrigg nature reserve, (d) S. Gosforth

Few samples exceeded the Dutch action or HPTULT values for soil Zn contamination. The HPTULT value was exceeded by three samples, one collected from each of the

Town Moor, Hazelrigg and S. Gosforth sites, the Dutch guideline being exceeded by only two samples, one from Hazelrigg and the second from S. Gosforth (Table 5.3).

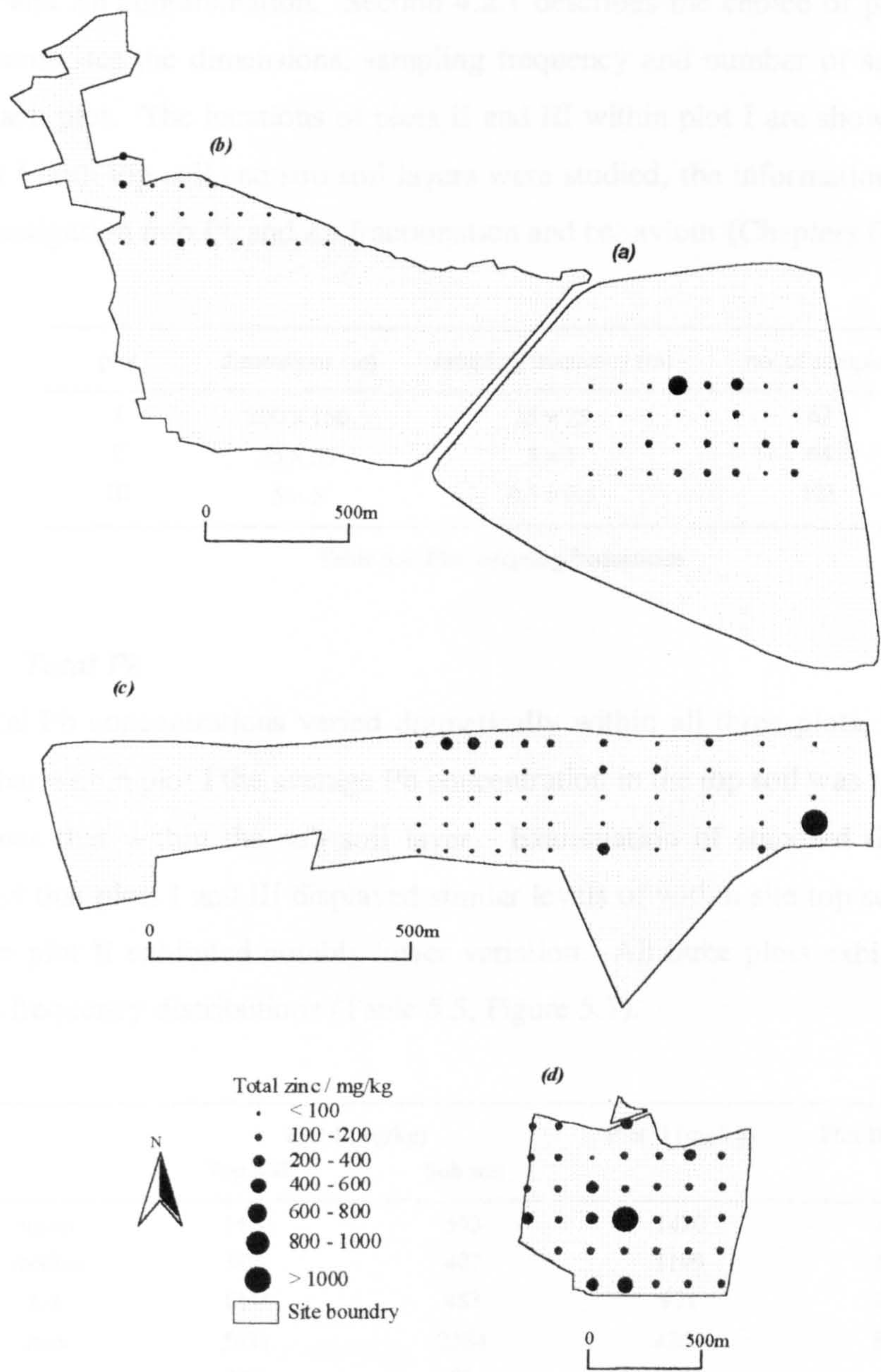


Figure 5.6 Site top soil total Zn concentration. (a) Town Moor, (b) Nuns Moor, (c) Hazelrigg nature reserve, (d) S. Gosforth

5.2.3 Plot scale: 25 × 25m to 0.5 × 0.5m

The strip of Pb contaminated land identified on Nuns Moor formed the location of the plot scale investigation. Three successively smaller plot areas were sampled on increasingly finer scales, providing more detailed information regarding the nature of the Pb and Zn contamination. Section 4.2.1 describes the choice of plot areas. Table 5.4 summarises the dimensions, sampling frequency and number of samples collected from each plot. The locations of plots II and III within plot I are shown in Figure 4.3. At plot I both top soil and sub soil layers were studied, the information being used for the investigation into Pb and Zn fractionation and behaviour (Chapters 6 and 7).

plot	dimensions (m)	sampling frequency (m)	no. of samples
I	200 × 150	25 × 25	63
II	35 × 35	5 × 5	64
III	5 × 5	0.5 × 0.5	121

Table 5.4 Plot sampling frequencies

5.2.3.1 Total Pb

Soil total Pb concentrations varied dramatically within all three plots, however it was noted that within plot I the average Pb concentration in the top soil was nearly two and a half times that within the sub soil layer. Examination of standard deviation values indicated that plots I and III displayed similar levels of within site top soil Pb variation, however plot II exhibited notably lower variation. All three plots exhibited positively skewed frequency distributions (Table 5.5, Figure 5.7).

	Plot I (mg/kg)		Plot II (mg/kg)	Plot III (mg/kg)
	Top soil	Sub soil		
mean	1450	593	1420	1543
median	906	407	1199	1231
s.d.	1244	483	971	1239
max	5631	2384	4264	8678
min	135	85	218	161
skewness	1.35	1.95	0.91	2.15

Table 5.5 Plots I, II and III summary statistics, Pb

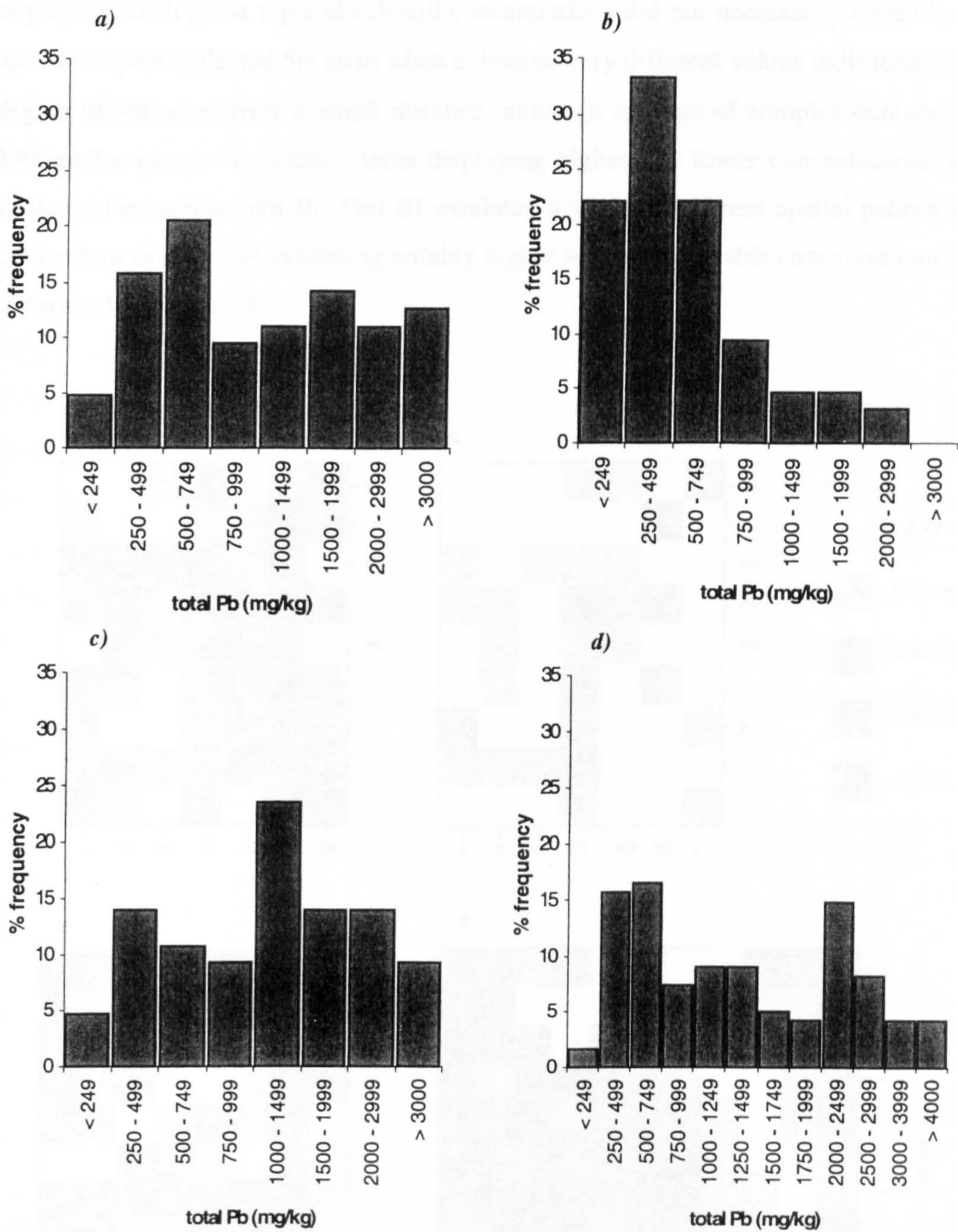


Figure 5.7 Plot total Pb concentrations, (a) Plot I, top soil, (b) Plot I, sub soil, (c) Plot II, (d) Plot III

In general the spatial distribution of Pb contamination appeared to be hot spot in nature, with isolated samples displaying high concentrations. This pattern was particularly evident in the sub soil layer of plot I. Within plot I it was noted that regions exhibiting higher top soil Pb also exhibited higher sub soil Pb, although individual sample points

displaying the highest top and sub soil concentrations did not necessarily coincide. At plot II samples collected 5m apart often exhibited very different values indicating a high degree of variation over a small distance, although clusters of samples containing $> 2000\text{mg/kg}$ were also noted. Areas displaying higher and lower concentrations were scattered throughout plot II. Plot III exhibited a slightly different spatial pattern with the western side of plot exhibiting notably higher and more variable concentrations than eastern side (Figure 5.8).

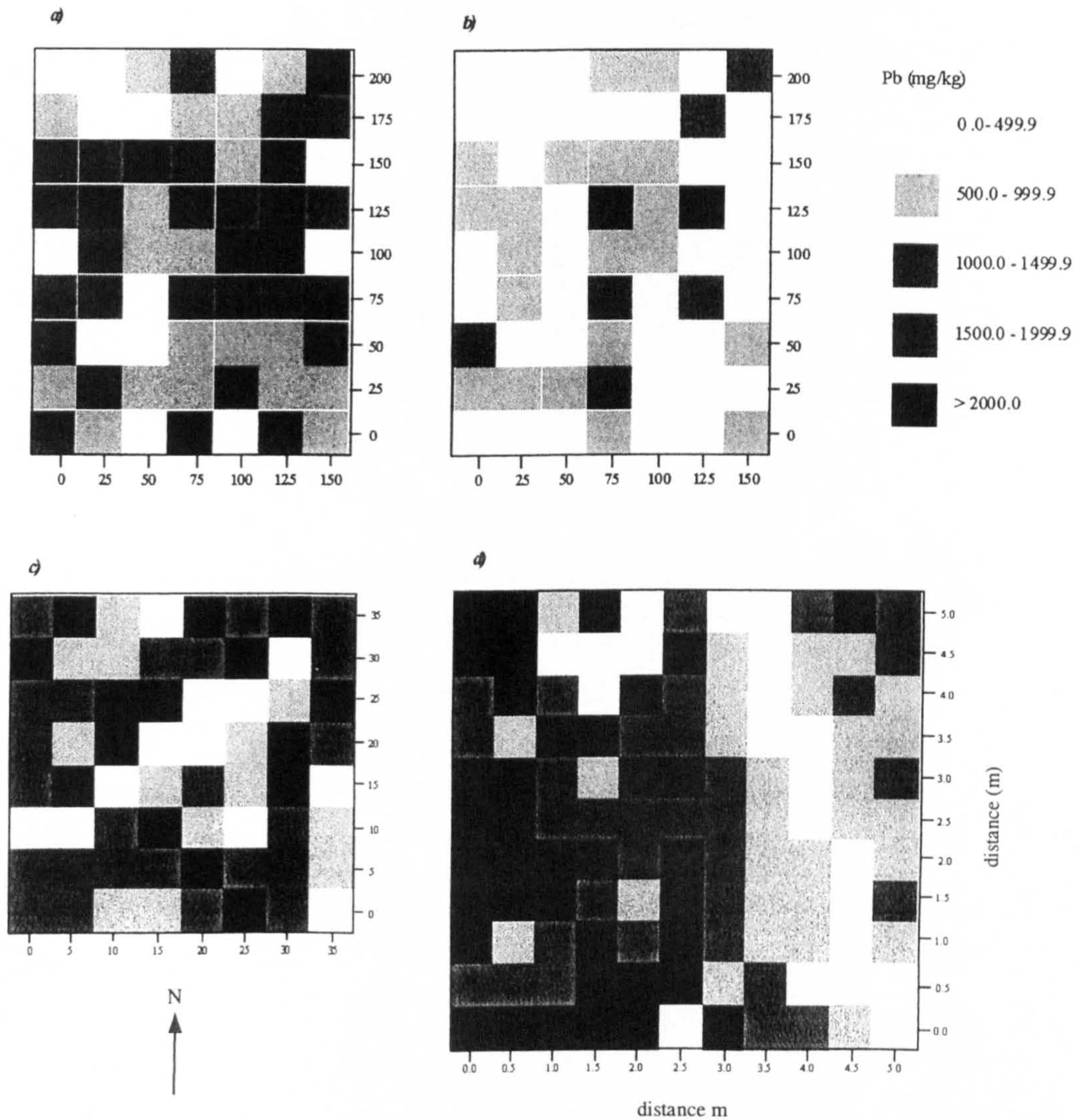


Figure 5.8 Spatial distribution, total Pb (a) Plot I top soil; (b) Plot I sub soil; (c) Plot II, (d) Plot III

Between 25 and 30% of top soil samples collected from each of the three plots exceeded the British ICRL trigger threshold for Pb concentrations within the soil of parks, playing fields and open spaces. This threshold was however, exceeded by only two plot I sub soil samples. 70 to 80% of top soil and 40% of sub soil samples exceeded the Dutch action guideline, whilst all samples, both top and sub soil, exceeded the Aspinall *et al.* (1988) HPTULT value.

5.2.3.2 Total Zn

Concentrations of soil total Zn were substantially lower than that of total Pb, the three plots exhibiting notably narrower ranges and lower mean Zn concentrations. Plots II and III displayed lower average top soil Zn concentrations than plot I in addition to lower standard deviation values. Plot I therefore exhibited the greatest within site variation. As with Pb, concentrations of Zn within the top soil layer of plot I were higher than within the sub soil layer, although in the case of Zn the difference was only marginal. Soil Zn concentrations displayed positively skewed frequency distributions (Table 5.6, Figure 5.9).

	Plot I (mg/kg)		Plot II (mg/kg)	Plot III (mg/kg)
	Top soil	Sub soil		
mean	76	601	59	69
Nadine	72	57	58	67
s.d.	26	18	17	18
max	184	155	114	120
min	46	43	35	34
skewness	2.48	3.62	1.08	0.68

Table 5.6 Plots I, II and III summary statistics, Zn

Soil Zn concentrations exhibited hotspot spatial variation, although the spatial variation was much simpler and less marked than the Pb contamination. Any variation was in the form of localised patches of either higher or lower concentrations; these areas were scattered throughout the three plots. Similarities were noted between the spatial variation of Zn concentrations within the top and sub soil layers of plot I (Figure 5.10).

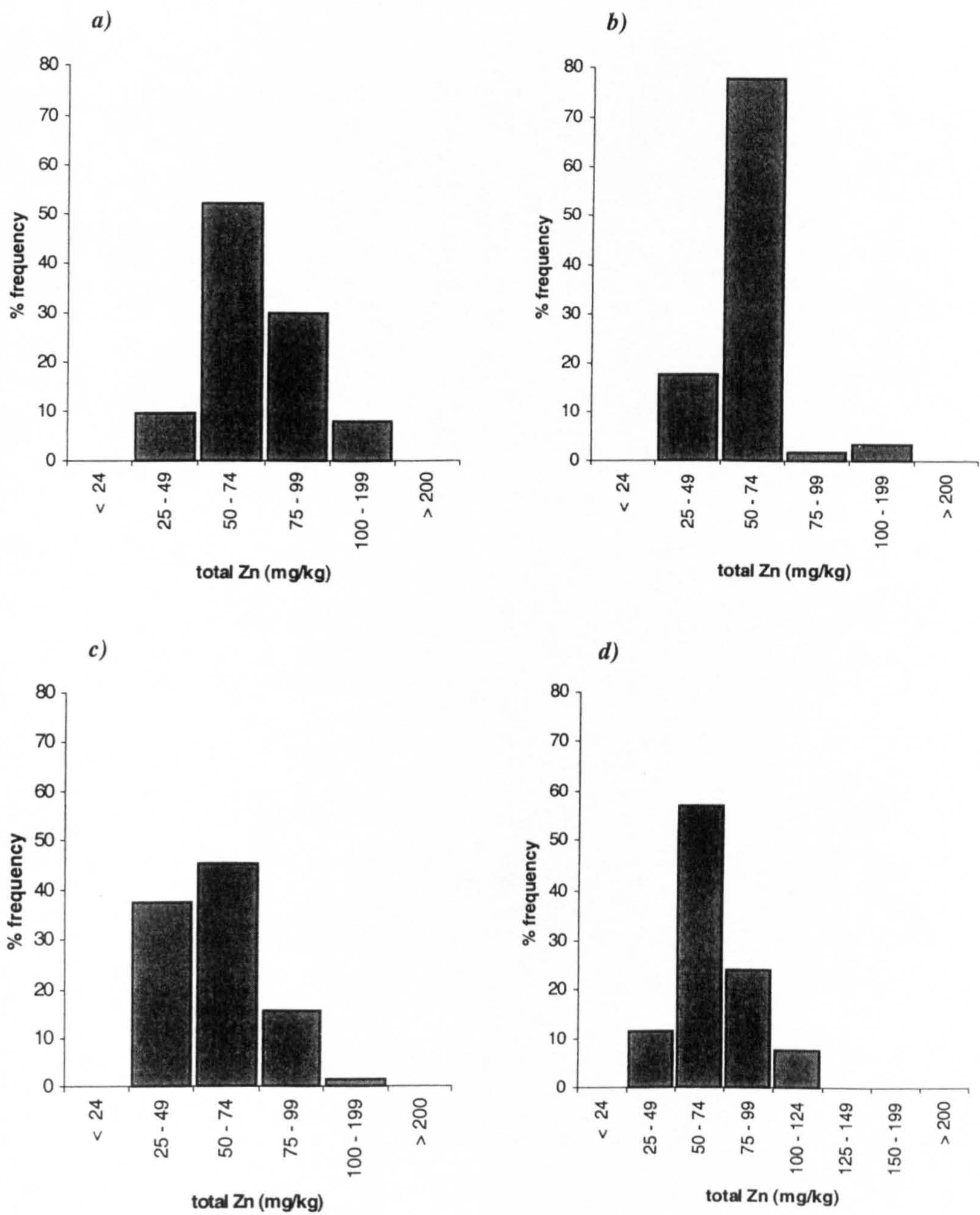


Figure 5.9 Plot total Zn concentrations, (a) Plot I, top soil, (b) Plot I, sub soil, (c) Plot II, (d) Plot III

All plot I, II and II samples were considered uncontaminated, containing concentrations of Zn well below the Dutch action and the HPTULT values.

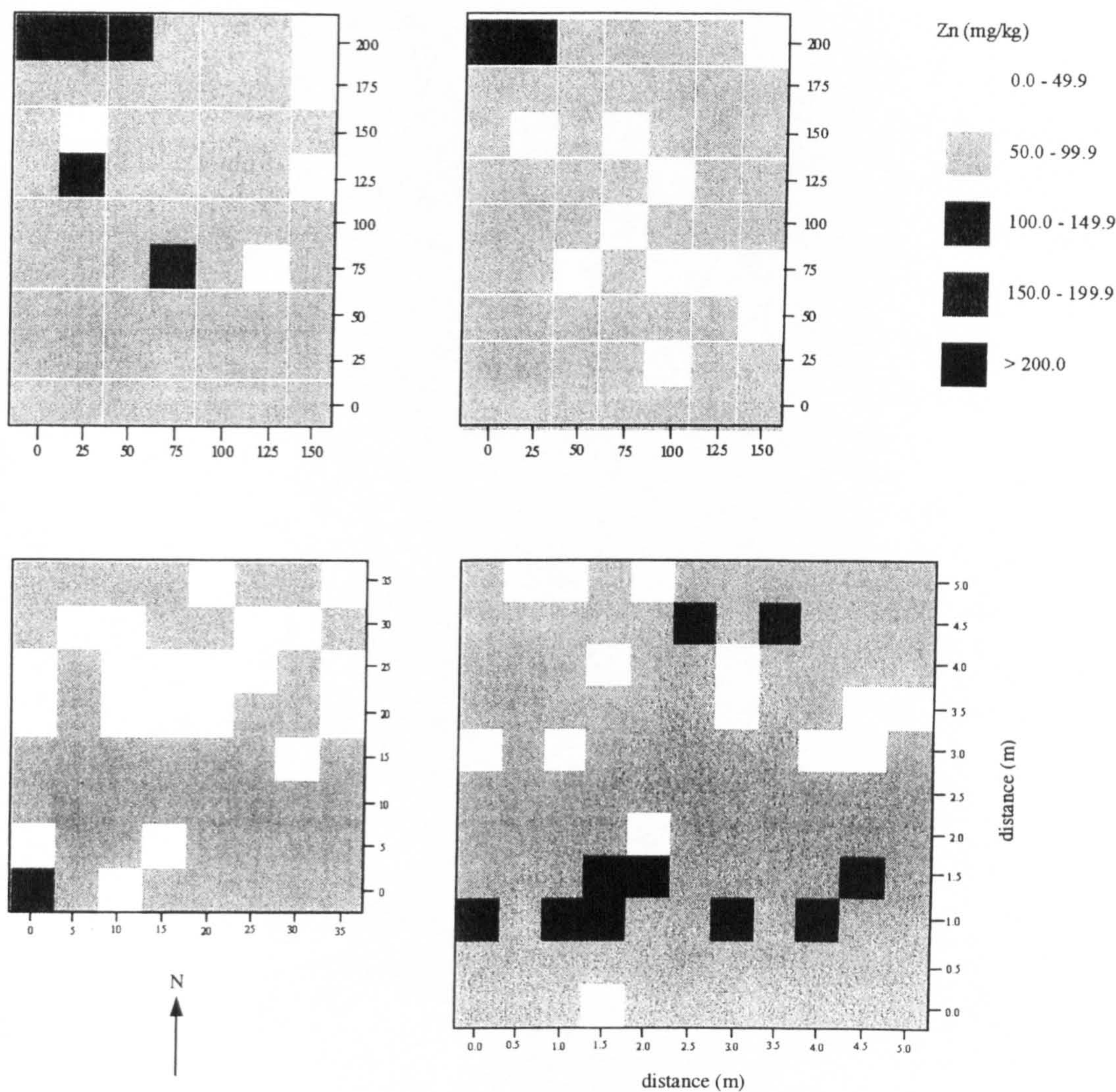


Figure 5.10 Spatial distribution, total Zn (a) Plot I top soil; (b) Plot I sub soil, (c) Plot II, (d) Plot III

5.3 SPATIAL DEPENDENCE

This section describes the spatial dependence / continuity between the samples of the three plot sites using both omni-directional and directional variograms. The variograms have been modelled using the method of least squares and the parameters, range, sill variance, nugget variance and gradient, used to determine the relationships between samples (Appendix 5). In addition to calculating individual variograms for the top and sub soil layers of plot I, the two layers were combined, assessing the affect of doubling

the number of samples on the resultant variogram. Data from all three plots have also been combined, producing a single variogram for each metal at the Nuns Moor site.

Following the rules of Journel and Huijbregts (1978), the size of the plots and number of samples collected determined the maximum reliable distance over which variograms could be calculated. Optimised lag spacings were determined as the shortest grid spacing for each plot with lag tolerance equal to half the lag spacing (Section 4.5.2.2). These parameters held for total Pb and Zn within all 3 plots (Table 5.7). Due to the small number of samples however, extra lags were examined prior to variogram modelling in order to confirm the validity of the chosen models. Prior to variogram analysis, data sets were examined and outliers removed. Those exhibiting skewness coefficients $> |1.0|$ were then subject to \log_{10} transformations (Section 4.5.2.1). Only plot III analysis could proceed past the calculation of omni-directional variograms as insufficient data were collected from the other two plots to accurately define anisotropy if it were to exist (Webster and Oliver, 1990; Oliver and Webster, 1991). Plot III directional variograms were calculated for 0° (N-S), 45° (NE-SW), 90° (E-W) and 135° (NW-SE) with an optimised angular tolerance of 22.5° (Section 4.5.2.2).

	maximum reliable distance (m)	optimised lag spacing (m)	optimised lag tolerance (m)	maximum no. of lags
Plot I	125.0	25.0	12.5	5
Plot II	24.7	5.0	2.5	5
Plot III	3.5	0.5	0.25	7
Plots combined	125.0	5.0	2.5	25

Table 5.7 Optimised omni-directional variogram parameters

5.3.1 Total Pb

5.3.1.1 Omni-directional variograms

At all three plots soil total Pb concentrations exhibited variograms that could be best modelled by linear functions (Table 5.8, Figures 5.11, 5.12 and 5.13), revealing similarities in the configuration of total Pb variation at all three sampling scales. The absence of variogram sills indicated that over the distances for which variograms had been calculated samples were still dependent upon each other. Substantial differences were noted in the semi-variances and slopes of the variograms, highlighting the existence of different levels of spatial dependence within the three plots. A steeper

gradient indicated a stronger spatial dependence between Pb concentrations within the top soil compared to the sub soil of plot I (Figure 5.11). However, it was noted that when the two soil layers were combined the resultant variogram exhibited a slope equal to approximately the average slope of the individual top and sub soil variograms (Figure 5.12). When combined, plot I top and sub soil Pb concentrations exhibited a similar level of spatial dependence to plot III Pb concentrations.

	model	range (m)	sill variance (γ)	slope	nugget variance (γ)
Plot I – top soil	linear	-	-	0.00026	0.1095
Plot I – sub soil	linear	-	-	0.00005	0.0340
Plot I – combined	linear	-	-	0.00014	0.1065
Plot II	linear	-	-	0.000005	0.1040
Plot III	linear	-	-	0.00014	0.0048
All Plots - combined	linear	-	-	0.00058	0.0980

Table 5.8 Omni-directional variogram parameters for plots I, II and III, total Pb

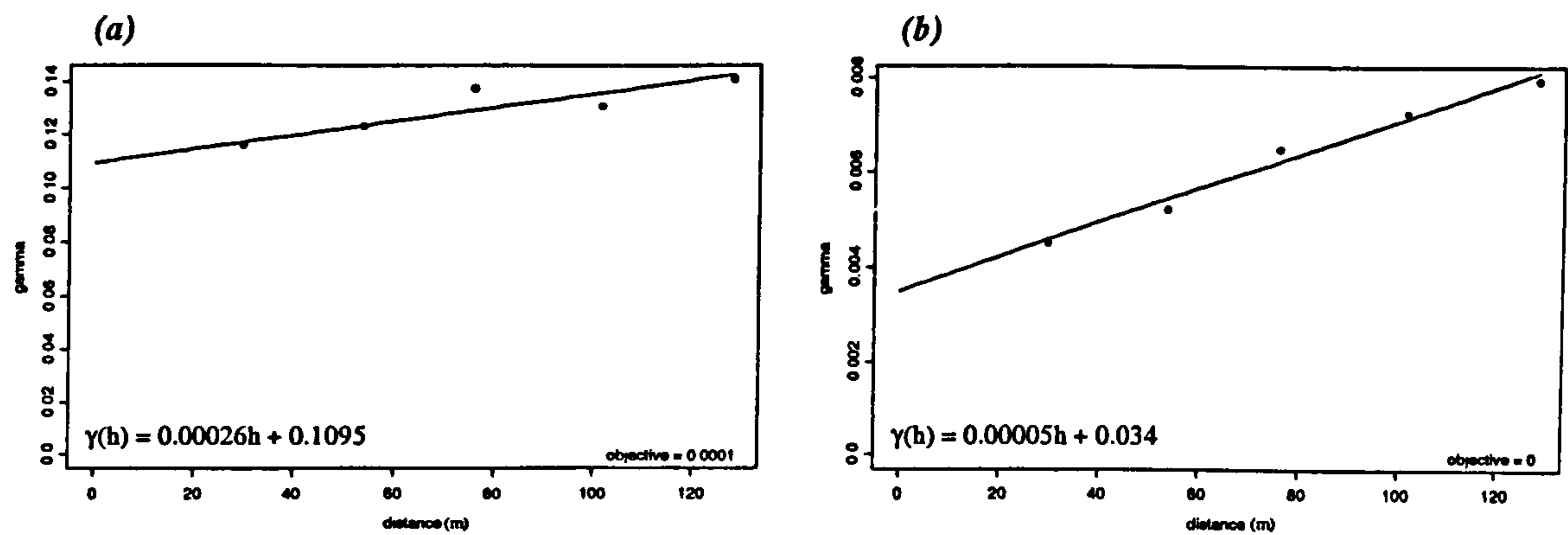


Figure 5.11 Omni-directional variograms, plot I (a) top soil total Pb, (b) sub soil total Pb

All variograms exhibited nugget variances indicating that a substantial degree of variation was occurring at distances less than the shortest lag. Moreover, plot II total Pb concentrations exhibited an almost purely nugget variogram, highlighting a weak relationship between samples collected 5m apart. A purely nugget variogram suggests either an absence of spatial structure or that spatial dependence may be occurring over a much smaller distance than that sampled, i.e. concentrations are exhibiting micro-heterogeneity. Despite this, the presence of linearly modelled variograms, calculated for samples collected on both a wider and narrower grid spacing than plot II, suggests

that spatial structure may not exist at the $5 \times 5\text{m}$ sampling scale. The existence of a substantial nugget variance at the plot III sampling scale ($0.5 \times 0.5\text{m}$) indicates that Pb concentrations are displaying little spatial structure and could possibly be considered as random (Figures 5.11, 5.12, 5.13).

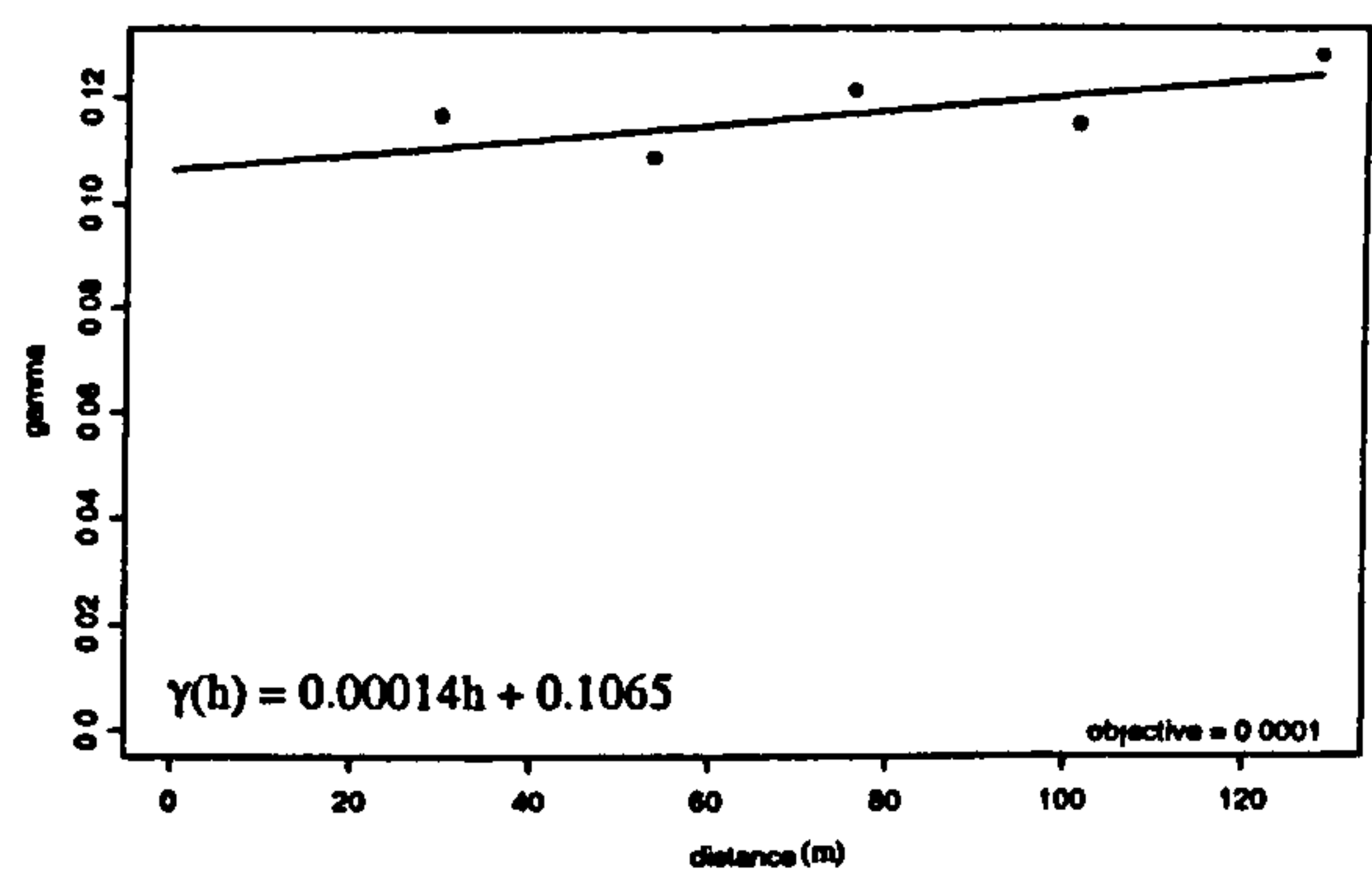


Figure 5.12 Omni-directional variogram, plot I, top and sub soil total Pb combined

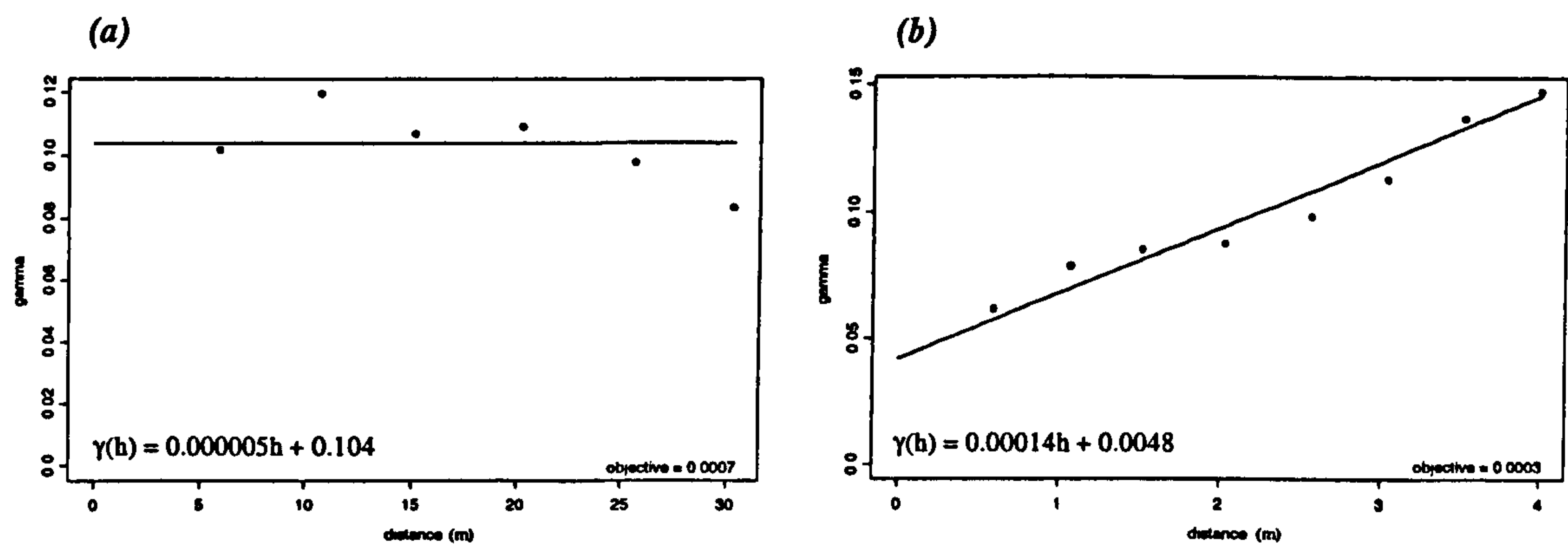


Figure 5.13 Omni-directional variograms, total Pb (a) plot II, (b) plot III.

Total Pb concentration data, when combined from all three plots to produce a single variogram of average lag distance 5m, was again best modelled by a linear function (Table 5.8, Figure 5.14). This variogram, exhibiting a steeper slope than the individual variograms, suggesting stronger spatial dependence, still displayed a substantial nugget variance. Notable variations in total Pb concentration were therefore occurring over a

distance shorter than the smallest lag spacing. Amalgamation of the data sets failed to improve variogram structure or reveal further information regarding the configuration of total Pb concentrations at the site. Again, the variogram highlighted spatial heterogeneity and micro-scale variation.

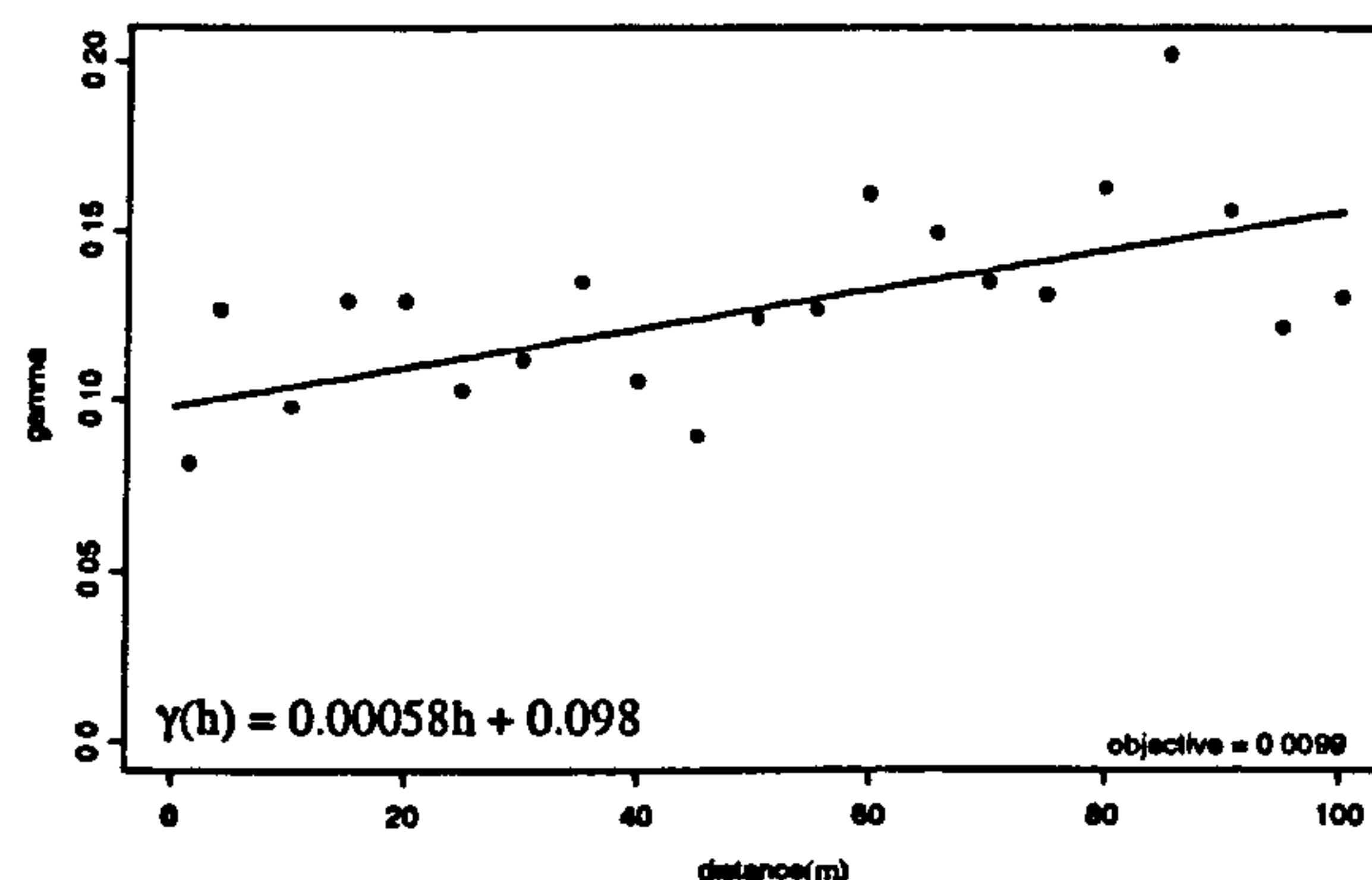


Figure 5.14 Omni-directional variogram, plots I, II and III combined, total Pb

5.3.1.2 Directional variograms

Directional variograms were produced for plot III data only, the $0.5 \times 0.5\text{m}$ sampling scale being the only scale sufficiently fine as to reveal a clearly structured omni-directional variogram (Figure 5.15). The use of fewer sampling points in the production of directional variograms determines that they will be of inherently less clear structure than omni-directional ones. In addition a suitably large number of sample points is required to accurately determine directional variograms.

All four directional variograms, 0° , 45° , 90° and 135° , calculated for plot III top soil total Pb concentrations were best fit by linear models (Table 5.9, Figure 5.15). A similar configuration was therefore revealed for total Pb variation within all directions. However, it was noted that variogram slopes varied marginally, indicating slight directional differences in the level of spatial dependence. Directions of maximum and minimum continuity were identified as 90° (E-W) and 0° (N-S), indicated by the steepest and most gentle variogram gradients, respectively. Lower semi-variances were noted in the 0° (N-S) direction indicating a greater similarity in Pb concentration in that direction. All four variograms exhibited similar nugget variances. The differences

observed within the variograms were marginal, hence Pb variation was assumed to be the same in all directions. Plot III was therefore treated as isotropic.

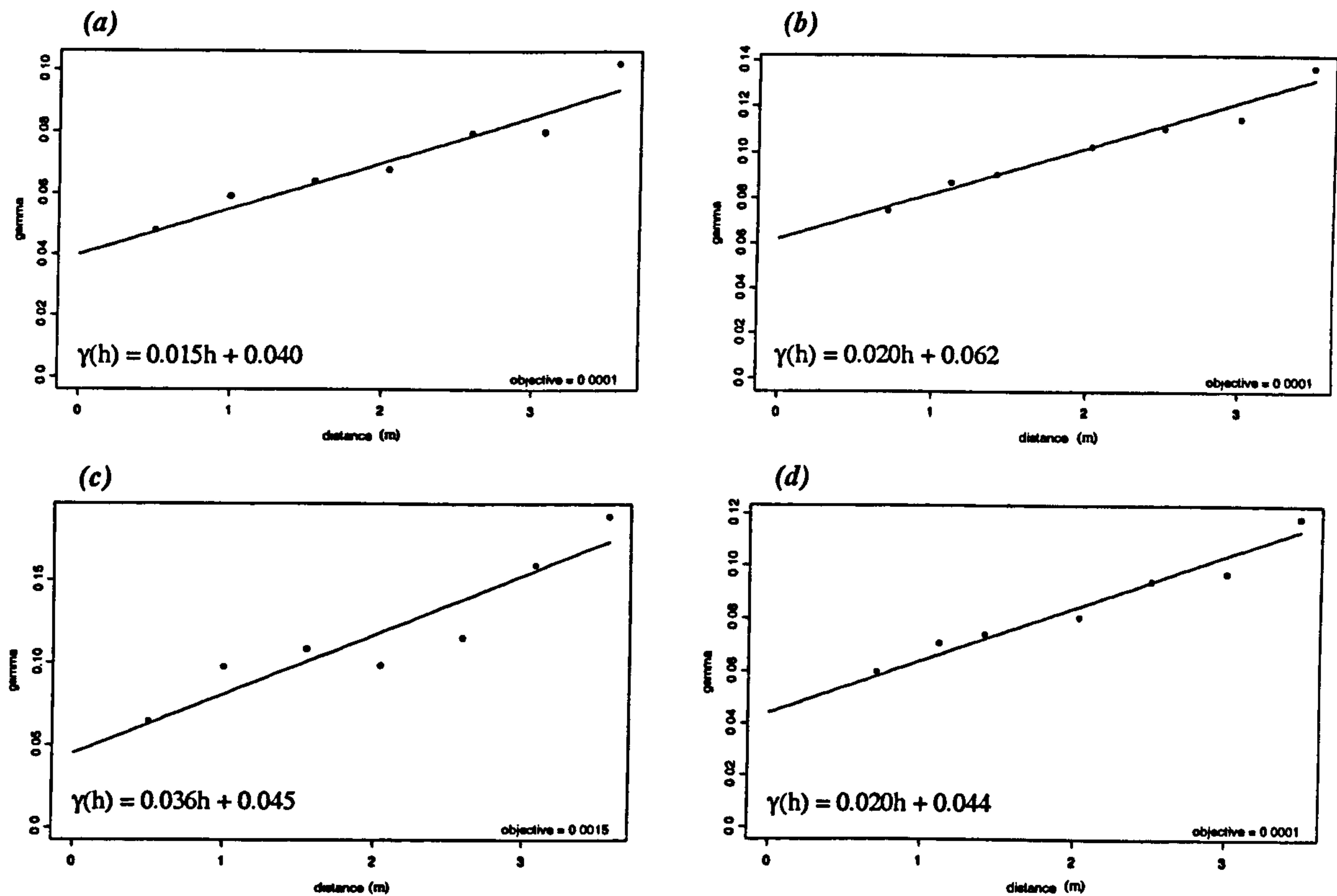


Figure 5.15 Directional variograms, plot III total Pb, (a) N – S (0°); (b) NE – SW (45°); (c) E – W (90°), (d) SE – NW (135°)

direction	model	range (m)	sill variance (γ)	slope	nugget variance (γ)
0° (N-S)	linear	-	-	0.015	0.040
45° (NE-SW)	linear	-	-	0.020	0.062
90° (E-W)	linear	-	-	0.036	0.045
135° (SE-NW)	linear	-	-	0.020	0.044

Table 5.9 Directional variogram parameters for plot III, total Pb

5.3.2 Total Zn

5.3.2.1 Omni-directional variograms

Plot I and II total Zn concentrations exhibited variograms that could be best modelled by linear functions, revealing similarities in the geographical configuration of Zn within the two plots (Table 5.10, Figures 5.16, 5.17 and 5.18). The absence of variogram sills indicated that, over the distance for which the variograms had been calculated samples were still dependent upon each other. It was noted that larger semi-variances, approximately a factor of 10 greater, were seen within the top than the sub soil of plot I suggesting that sub soil Zn concentrations were less variable than top soil Zn concentrations. These differences were also reflected in the gradients of the variograms. When data from the two layers of plot I were amalgamated the resultant variogram was best fit by a bounded type spherical model of range 110m (Table 5.10, Figure 5.17). A clearer structure was therefore identified when more data points were included within the analysis, the variogram revealing the distance at which Zn concentrations became independent. Nugget variances indicated that variation was occurring at a distance less than the shortest sampling interval.

	model	range (m)	sill variance (γ)	slope	nugget variance (γ)
Plot I – top soil	linear	-	-	0.000036	0.0055
Plot I – sub soil	linear	-	-	0.000014	0.0021
Plot I – combined	spherical	110	0.0029	-	0.0044
Plot II	linear	-	-	0.026	0.1040
Plot III	spherical	1.9	0.0054	-	0.0054
All Plots - combined	linear	-	-	0.000	0.010

Table 5.10 Omni-directional variogram parameters for plots I, II and III, total Zn

A different geographical configuration was revealed within plot III, where top soil total Zn exhibited a bounded type variogram best fit by a spherical model (Table 5.10, Figure 5.18). The model exhibited a small range, indicating that soil Zn concentration was spatially dependent over a short distance, approximately 2m. A substantial nugget variance, approximately half the total variance, indicated that notable variation was occurring at a distance less than the shortest sampling lag, possibly reflecting micro-scale variations in metal concentration.

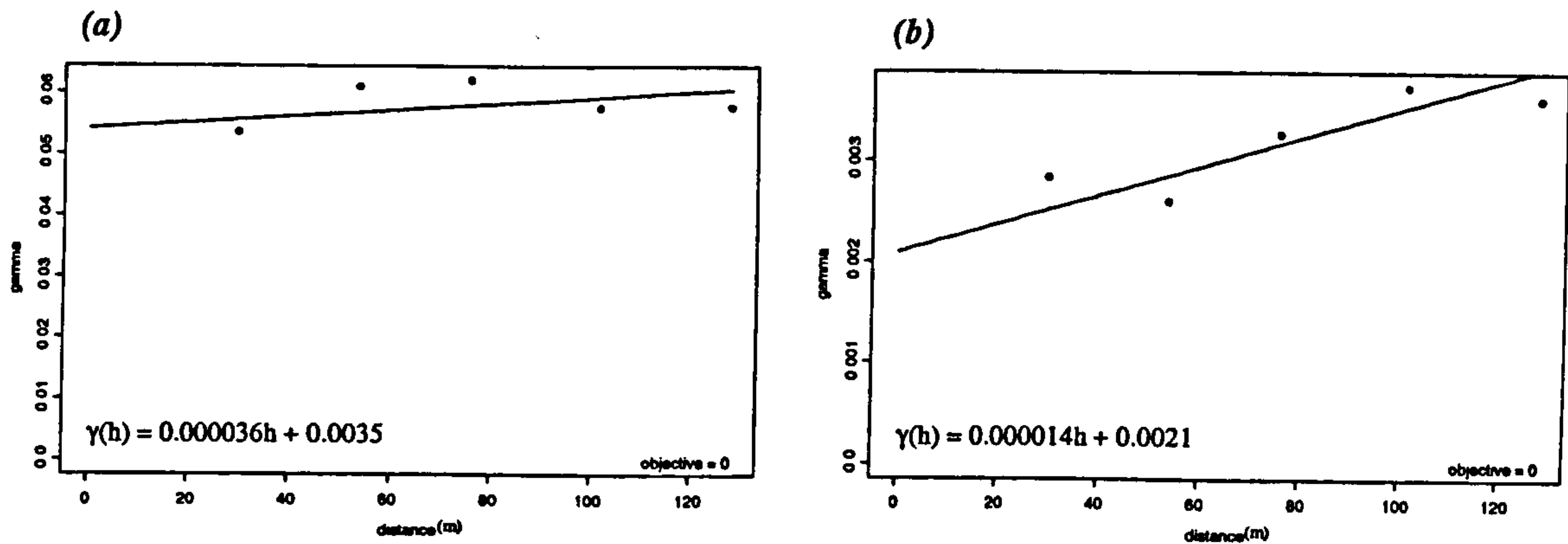


Figure 5.16 Omnidirectional variograms, plot I (a) top soil total Zn, (b) sub soil total Zn

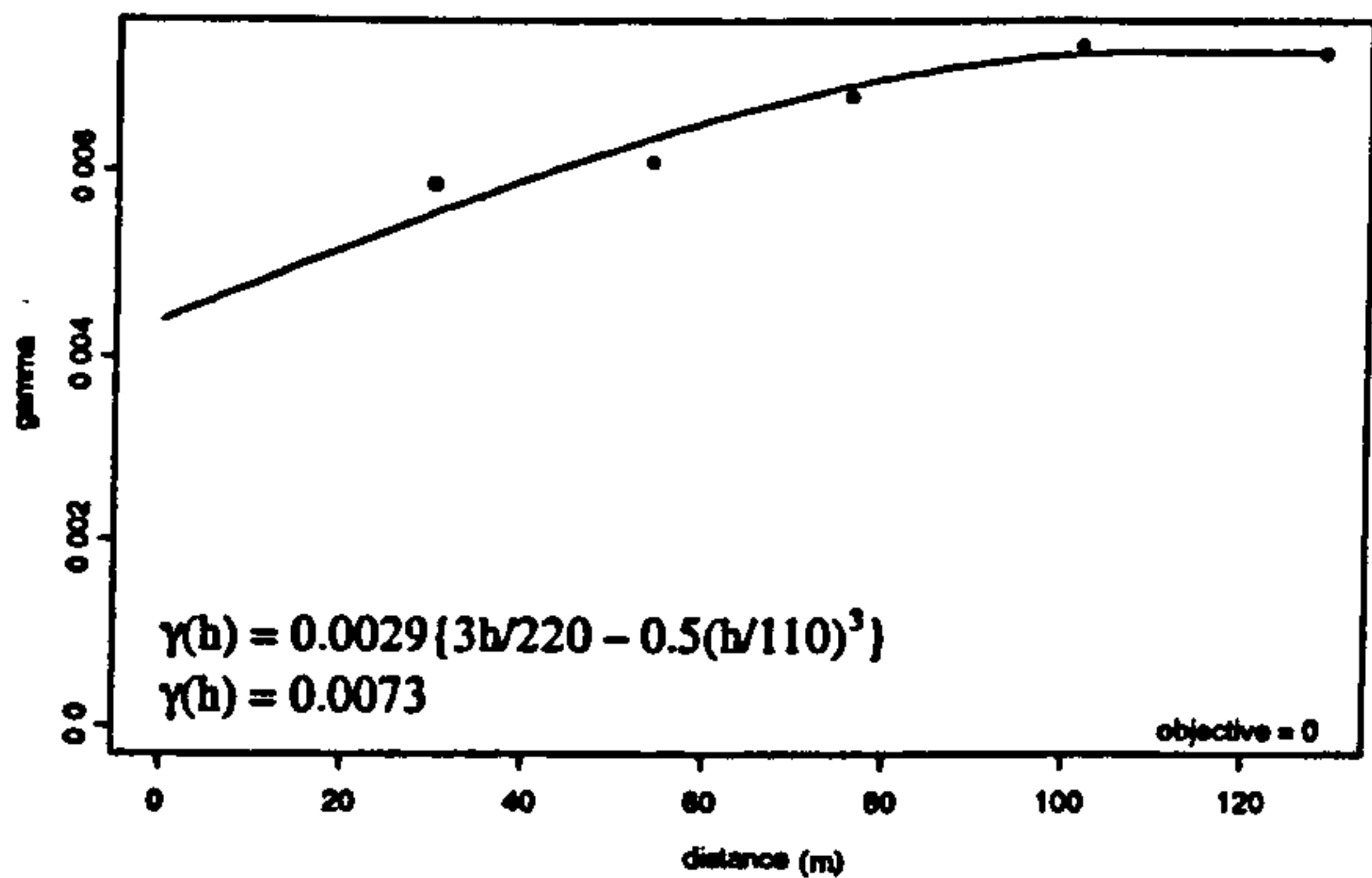


Figure 5.17 Omnidirectional variogram, plot I, top and sub soil total Zn combined

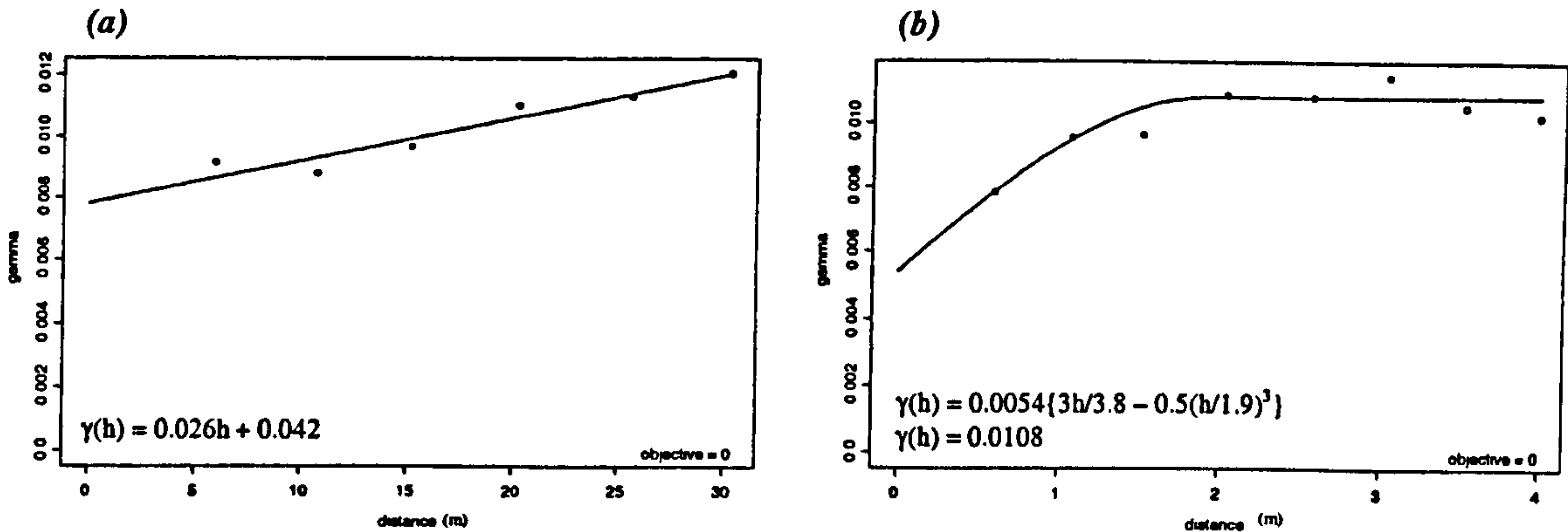


Figure 5.18 Omnidirectional variograms, total Zn (a) plot II, (b) plot III

Amalgamation of the plot I, II and III data sets for total Zn resulted in the formation of a purely nugget variogram (Table 5.10, Figure 5.19). The variogram, produced for an average lag spacing of 5m, indicated a lack of spatial structure to soil Zn concentrations, at this scale. As the plot III variogram ($0.5 \times 0.5\text{m}$ scale) exhibited a relatively clear structure, the previous result indicates that spatial dependence may be occurring over a smaller distance than the shortest lag spacing 5m, calculated for the combined data sets. This result suggests the occurrence of micro-scale Zn heterogeneity within the soil.

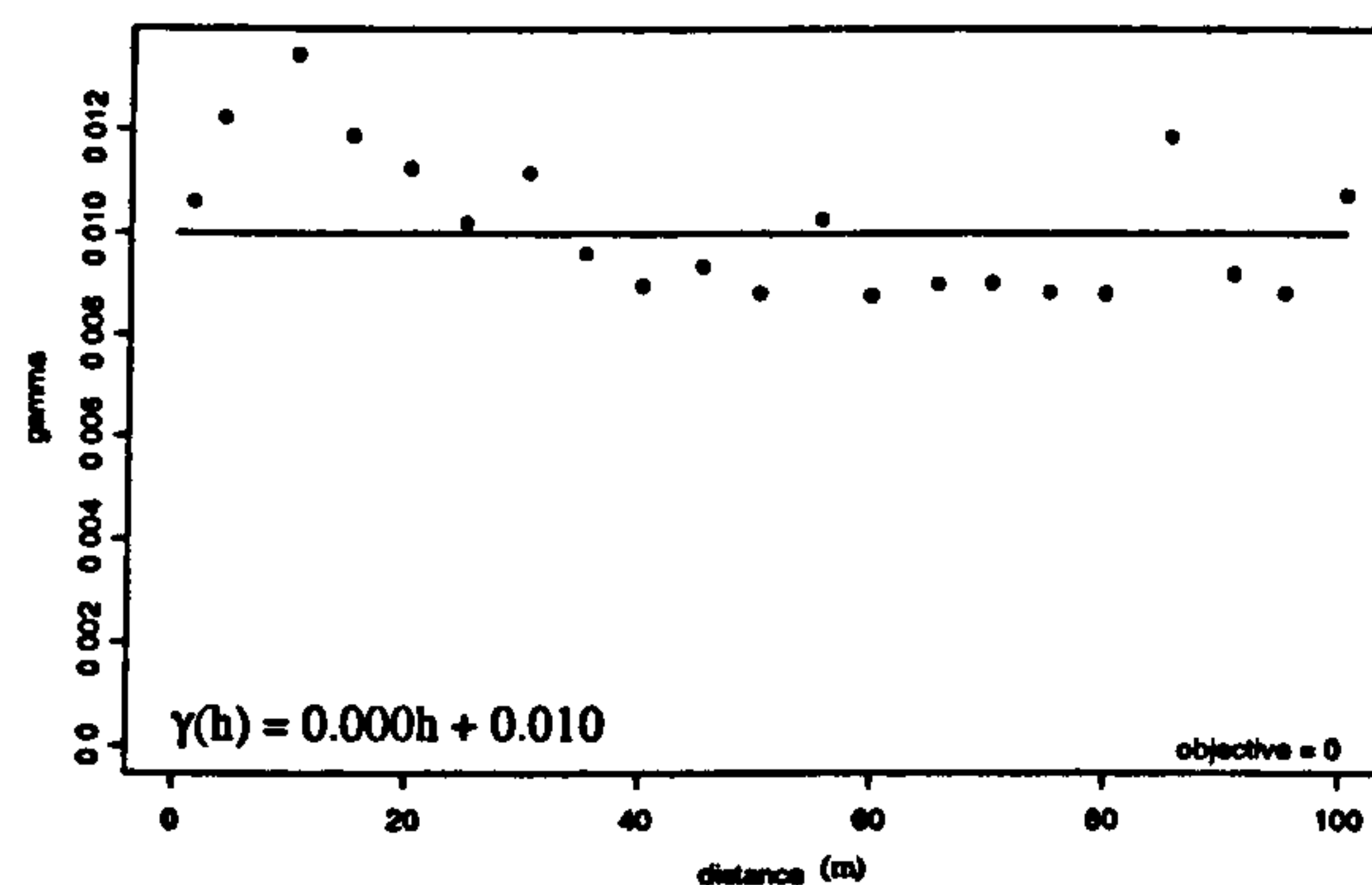


Figure 5.19 Omni-directional variogram, plots I, II and III combined, total Zn

5.3.2.2 Directional variograms

Directional variograms, determined for plot III total Zn, exhibited relatively clear well-behaved structures. The 0° (N-S) and 135° (SE-NW) variograms were best modelled by spherical functions whilst the 45° (NE-SW) and 90° (E-W) variograms were best fit by linear functions (Table 5.11, Figure 5.20). The two spherical variograms, 0° and 135° , displayed ranges of 1.25 and 2.70m, hence Zn concentrations in the SE-NW direction were spatially dependent for a longer distance than in the N-S direction. It was noted that the 90° variogram exhibited marginally lower semi-variances than the other three variograms indicating that Zn concentrations in the E-W direction were most similar. With the exception of the 0° variogram all displayed substantial nugget variances. Despite slight differences in the directional variograms, the distance over which they had been calculated was small, therefore the plot was assumed to be isotropic and the omni-directional variogram used for further analysis.

direction	model	range (m)	sill variance (γ)	slope	nugget variance (γ)
0° (N-S)	spherical	1.25	0.0101	-	0.002
45° (NE-SW)	linear	-	-	0.0016	0.0075
90° (E-W)	linear	-	-	0.00046	0.007
135° (SE-NW)	spherical	2.70	0.006	-	0.0063

Table 5.11 Directional variogram parameters for plot III, total Zn

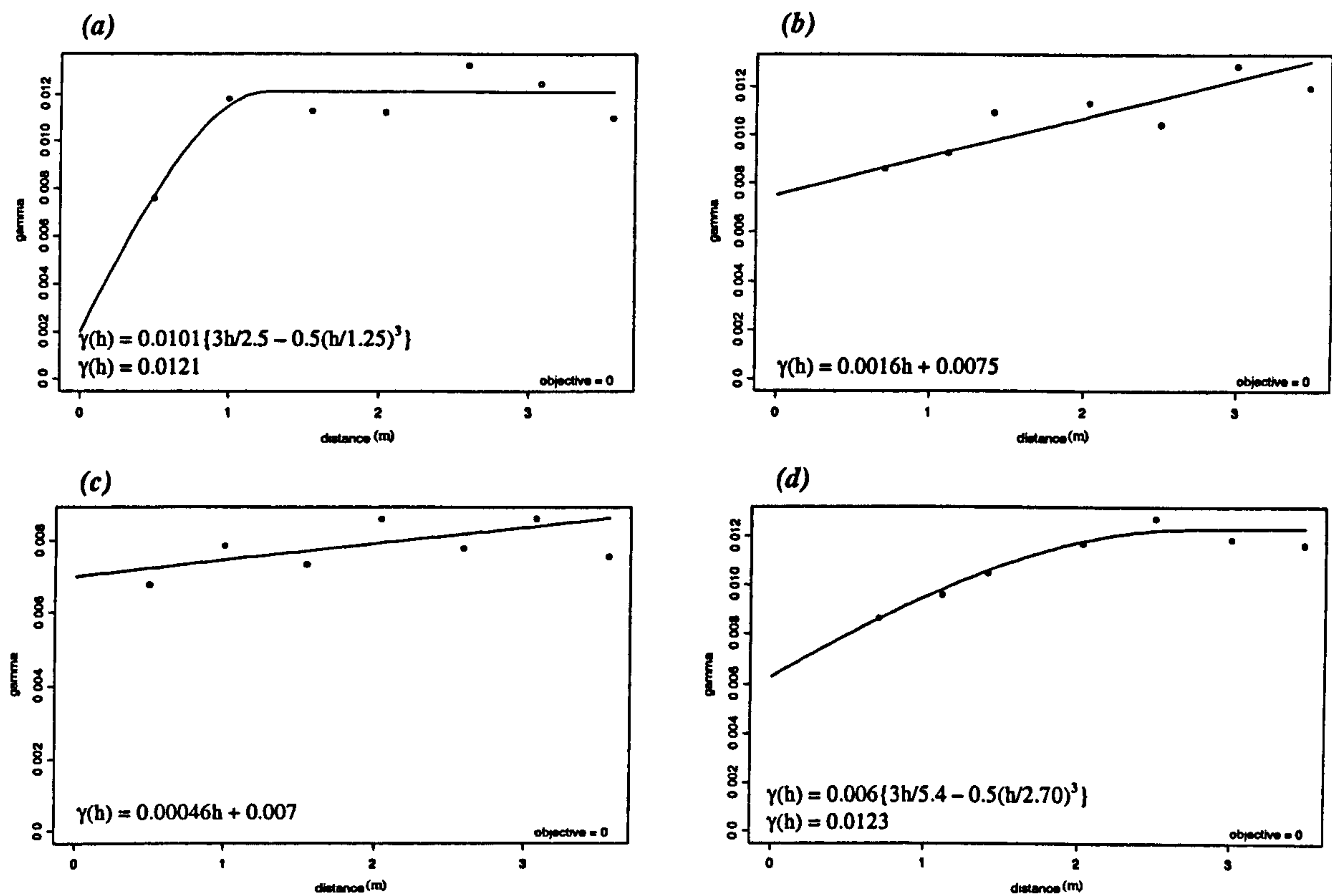


Figure 5.20 Directional variograms, plot III total Zn, (a) N – S (0°); (b) NE – SW (45°); (c) E – W (90°), (d) SE – NW (135°)

5.4 SURFACE INTERPOLATION

A surface interpolation was produced for the total Zn concentration within the soil of plot III using the variogram parameters determined in section 5.3.2.1 and punctual kriging. An interpolation could not be produced for total Pb as the variogram was best fit by a linear model. The omni-directional variogram was used as differences between the directional variograms were relatively small (Section 5.3.2.2), indicating the

existence of negligible anisotropy. In addition, insufficient sample points were available to enable directional variograms to be entirely reliable (Section 4.5.2.2). Surface interpolation provides a method whereby estimates of non-sampled areas may be made within a sampled area. Predictions were produced on a 40 × 40 grid, offset from the sample points by 0.125m.

Total Zn concentrations interpolated using the method of punctual kriging produced a similar pattern to that exhibited by the pixel map of the surface plot (Figure 5.10). Interpolations were produced using the spatial statistics module of S-Plus. Default prediction grid spacings were used, as when tested prediction grid spacing was seen to exhibit little effect on the standard errors produced (Table 5.12)

	20 × 20 (≈0.26m ²)	30 × 30 (≈0.17m ²)	40 × 40 (≈0.13m ²)	50 × 50 (≈0.10m ²)
mean	0.0873	0.0877	0.0879	0.0880
median	0.0894	0.0893	0.0893	0.0894
max.	0.1036	0.1037	0.1038	0.1038
min.	0.0000	0.0000	0.0000	0.0000

Table 5.12 Summary of kriging prediction standard errors for prediction point grids of varying sizes.

As previously identified (Section 5.2.3.2) peaks of higher total Zn concentration were seen towards the four corners of the plot. The two highest peaks were identified in the north western and south western corners. Lowest concentrations were identified in a central band running north – south across the area (Figure 5.21). Prediction standard errors were seen to increase from zero at the sample points to a maximum at the centre of each grid square, a pattern typical of ordinary kriging (Webster and Oliver, 1990). The greatest errors were seen at the corners and edges of the plot, i.e. areas not completely surrounded by neighbouring samples, and in the vicinity of those samples removed to maintain the condition of stationarity (Section 4.5.2.2). The higher errors were a result of reduced influence from certain directions.

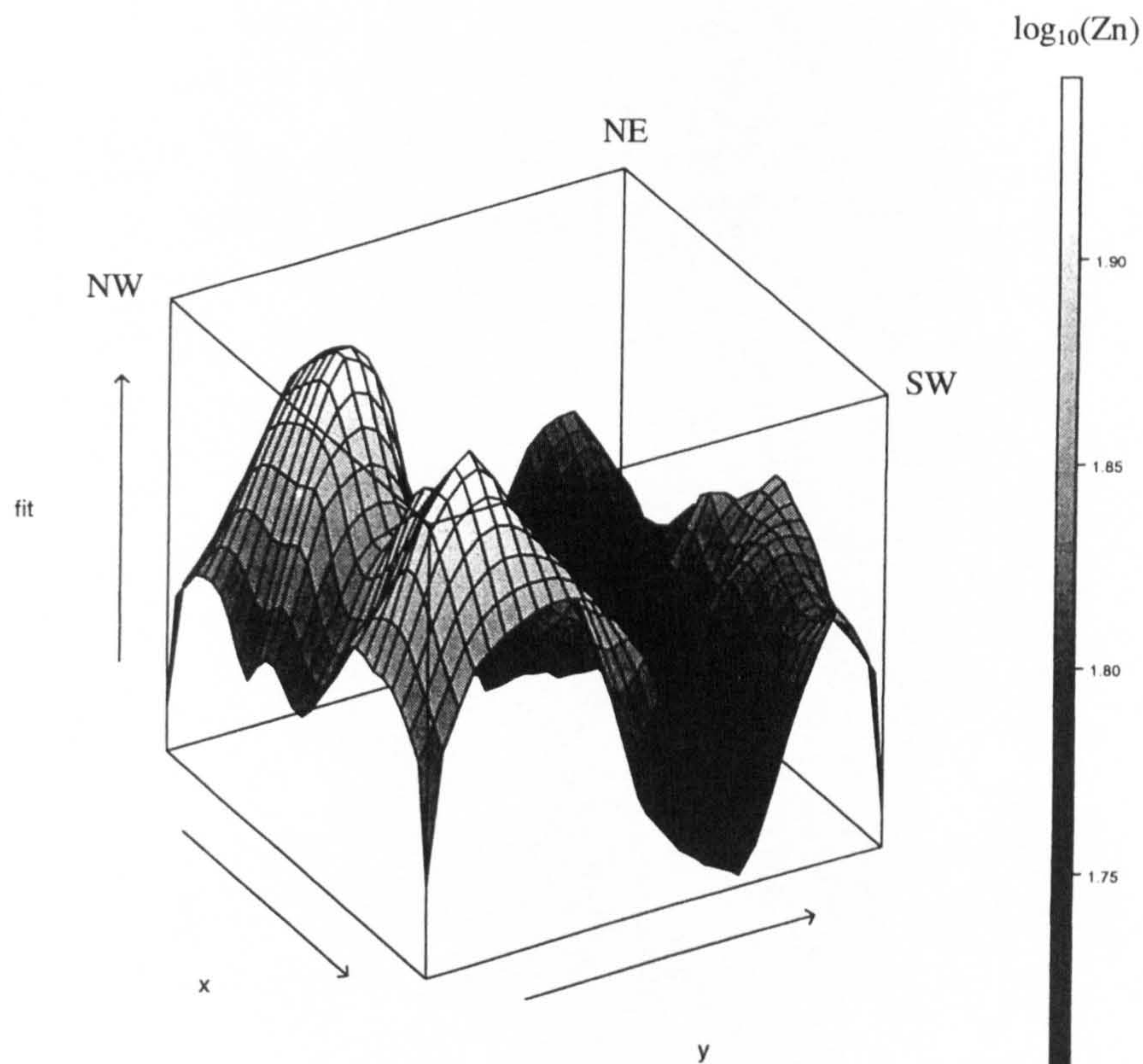


Figure 5.21 Surface interpolation of top soil Zn concentrations, plot III

5.4 SUMMARY

The four sites and three plots all displayed higher levels of soil total Pb and Zn contamination, although a high degree of concentration variation was noted for both metals. The samples collected on the finest scale ($0.5 \times 0.5\text{m}$) exhibited as great if not greater variation than those collected on all sampling scales (Section 5.2). Sampling on a relatively coarse scale was seen therefore to simplify soil Pb and Zn contamination. All data sets exhibited positively skewed frequency distributions, displaying large numbers of low and few high concentrations. Spatial distribution was hot spot or localised in nature, with samples displaying high concentrations often surrounded by others of low concentration. Such phenomena are often typical of geochemical data sets.

The omni-directional variograms determined for plots I, II and III displayed varying structure and parameters, however the majority were best fit by linear models. The different parameters indicated different levels of spatial dependence (Section 5.3). Variograms produced for plots I and II exhibited a less clear structure than those of plot III. The plot III total Zn concentration was best fit by a bounded type model enabling spatial dependence to be determined for Zn within plot III. The presence of nugget variances at all sampling scales gave indications of micro-scale variation in soil Pb and Zn concentrations, suggesting that even finer sampling would be required to determine the true structure of the variograms. Very similar directional variograms calculated for plot III indicated that Pb and Zn variation was isotropic. In addition, too few samples had been collected for a full exploration of anisotropy (Webster and Oliver, 1991).

The surface interpolation produced for total Zn within plot III (punctual kriging) exhibited the same general form as the pixel map. An interpolation could not be conducted for total Pb. Kriging utilises the relationship between sampling points by assigning weights to neighbouring values hence predictions are more accurate. The largest errors were seen at the corners of the plot in addition to those areas where outlying values had been removed to maintain the assumption of stationarity (Section 4.5.2.2).

CHAPTER 6

FRACTIONATION OF Pb AND Zn

Summary

This chapter investigates the forms in which the metals (Pb and Zn) are held within the soil system at Plot I. Emphasis has been placed on spatial variation, partitioning and enrichment within the top and sub soil layers. The chapter has been divided into 6 main sections. Section 6.1, the introduction, outlines the analyses conducted within the chapter. Sections 6.2 and 6.3, respectively, describe Pb and Zn fractionation and partitioning between four fractions, exchangeable, reducible, oxidisable and residual, as determined using the BCR sequential extraction technique. The analysis focuses on both concentration and spatial variation. Section 6.4 examines the spatial continuity of the fractions using variograms. Enrichment ratios (top soil : sub soil concentrations) are examined in section 6.5, again with emphasis on variation. Section 6.6 concludes the chapter, reiterating the main findings and identifying areas for discussion in chapter 8.

6.1 INTRODUCTION

This chapter describes the partitioning of the metals Pb and Zn between four different fractions: exchangeable, reducible, oxidisable and residual, determined using the BCR sequential extraction technique (Davidson *et al.*, 1994) (Section 4.3.1, Appendix 2). The BCR technique was chosen for this investigation as a substantial degree of research has been conducted to assess both the reproducibility and efficiency of this method, the aim being to develop a universal technique of sequential extraction. The investigation, conducted on a 25 × 25m scale at plot I, studies both top soil and sub soil fractionation, examining concentration, spatial variation and partitioning (Sections 6.2 and 6.3), in addition to top : sub soil enrichment ratios (Section 6.5). A picture of the forms, potential availability and toxicity has therefore been determined for this plot site.

6.2 Pb FRACTIONATION

Sequential extraction determined that the soil of plot I contained variable concentrations of the four different forms of Pb. These listed in order of availability are exchangeable > reducible > oxidisable > residual. For each sample, the sum of the four fractions was approximately 86% of the total metal extracted using the microwave technique (Appendix 3). Using means, medians, ranges and measures of skewness in conjunction with frequency distributions and concentration plots this section describes the concentrations, spatial variation and partitioning of the metal fractions within both the top and sub soil layers of plot I (Section 4.5.1).

6.2.1 Top soil

The four Pb fractions exhibited dramatically varying concentrations, with the highest degree of variation being noted within the reducible and oxidisable fractions. The most readily available, exchangeable fraction exhibited the lowest mean concentration although this was only marginally lower than that displayed by the least available, residual fraction. On average samples contained approximately 5 to 6 times more reducible and oxidisable Pb than either exchangeable or residual Pb. As highlighted by the concentration differences a substantially greater proportion of the top soil total Pb was of the reducible and oxidisable forms. All four fractions exhibited positively skewed concentration distributions, although it was noted that the proportion of reducible Pb exhibited a negatively skewed distribution (Table 6.1, Figures 6.1 and 6.2).

	Pb	exchangeable	reducible	oxidisable	residual	sum
(mg/kg)	mean	106	549	644	128	1427
	median	60	369	423	93	963
	s.d.	107	485	514	119	1184
	max.	491	1962	2029	783	4975
	min.	3	34	45	21	131
	skewness	1.37	1.31	1.17	3.19	1.26
(%)	mean	6.5	36.8	46.4	10.3	-
	median	5.7	38.0	45.3	9.2	-
	s.d.	3.2	5.5	6.7	4.9	-
	max.	17.0	45.7	64.1	37.8	-
	min.	1.6	23.5	30.6	4.3	-
	skewness	0.90	-0.50	0.37	3.11	-

Table 6.1 Plot I summary statistics, top soil Pb

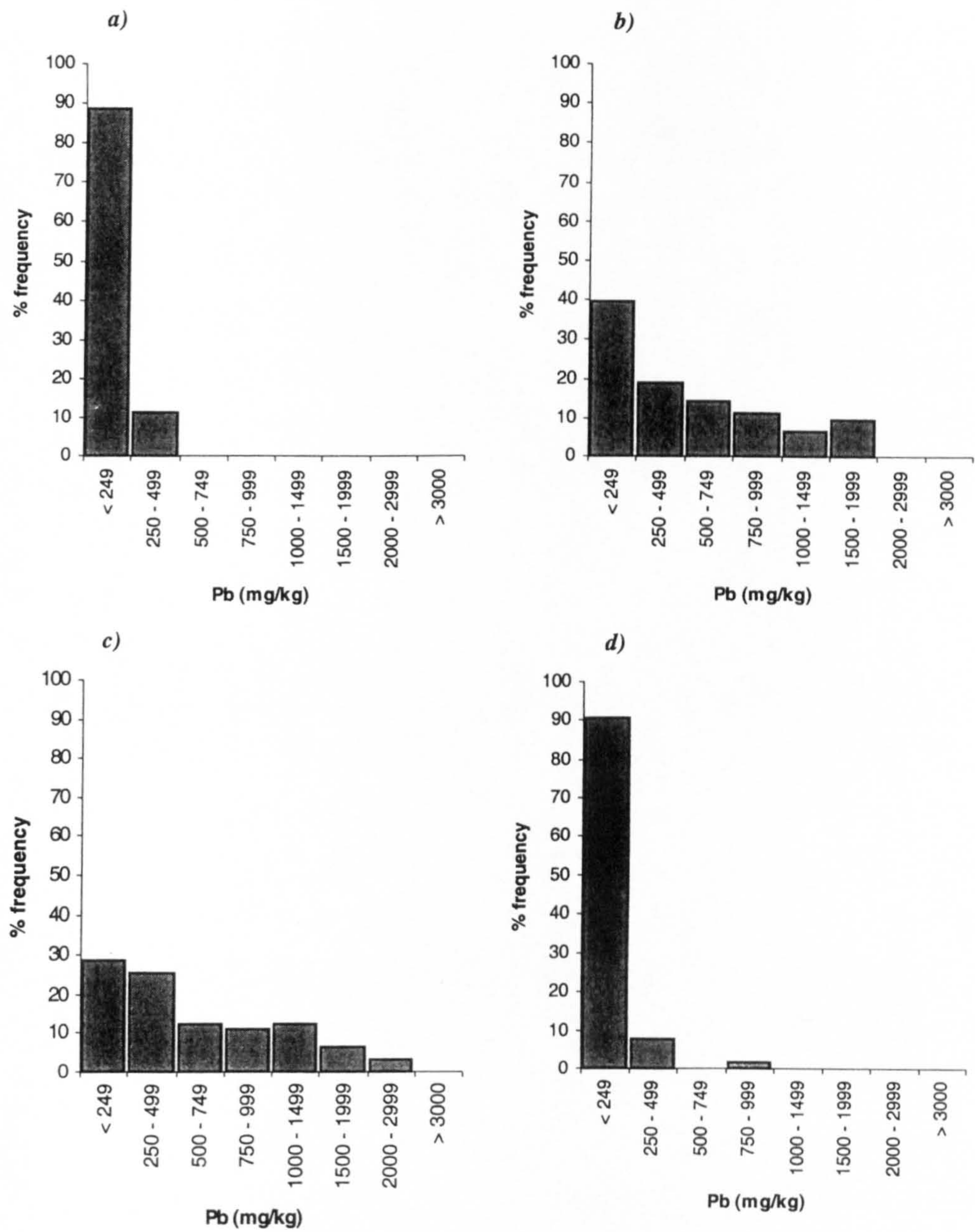


Figure 6.1 Frequency distribution of Pb fractions, top soil (a) exchangeable; (b) reeducible; (c) oxidisable; (d) residual

All four fractions exhibited a similar pattern of spatial distribution which was closely related to that of the total metal (Figures 6.3 and 5.8). In general, the pattern was hotspot in nature with high and low concentrations located within similar areas. The spatial distribution of the two most variable fractions appeared to be very closely related

with samples exhibiting > 1000mg/kg of reducible Pb also exhibiting > 1000mg/kg of oxidisable Pb. Some of these samples also displayed higher concentrations of exchangeable and residual Pb (Figure 6.3).

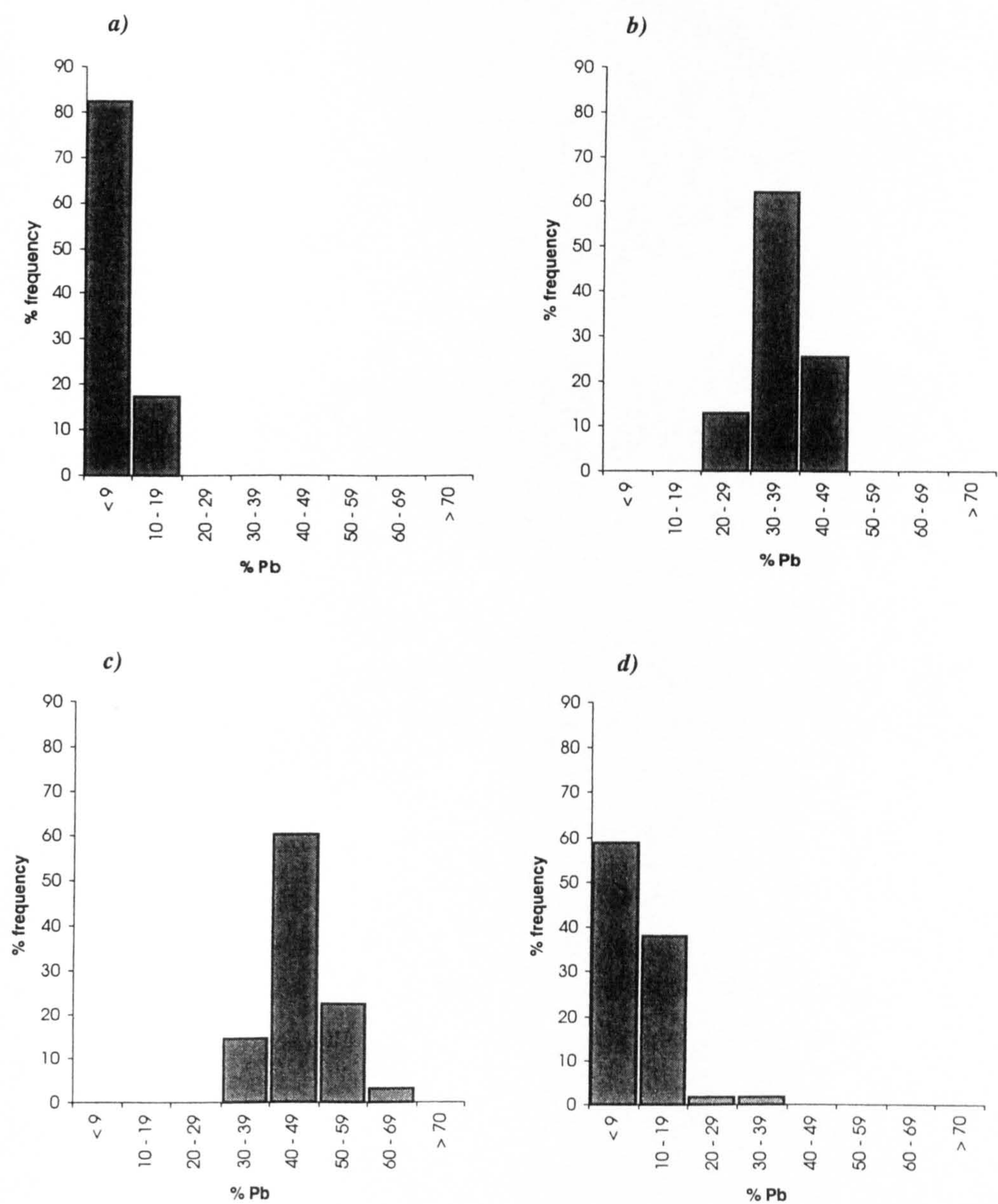


Figure 6.2 Pb partitioning, top soil (a) exchangeable; (b) reducible; (c) oxidisable; (d) residual

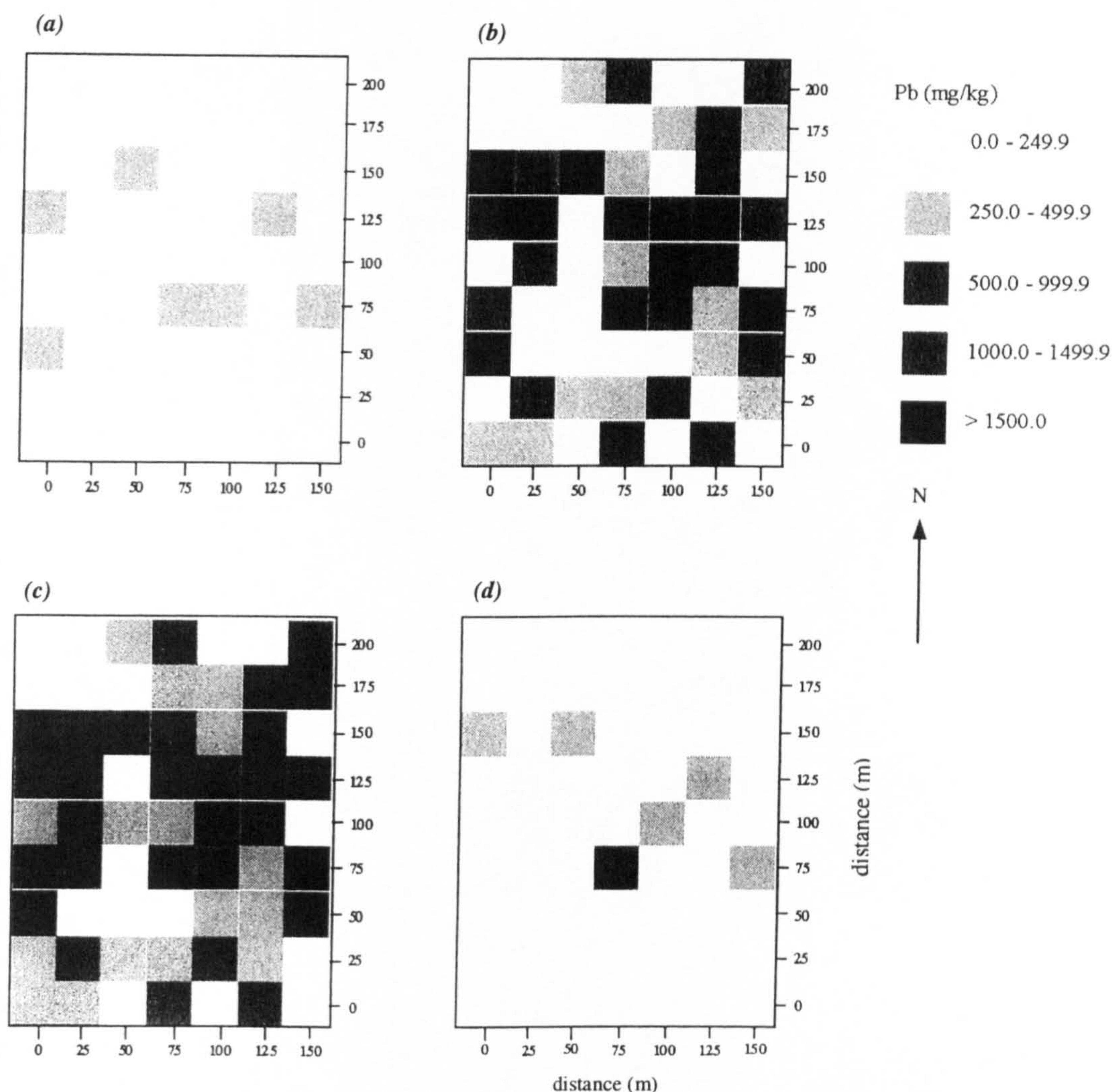


Figure 6.3 Spatial distribution, Plot I top soil Pb fractions (a) exchangeable; (b) reducible, (c) oxidisable, (d) residual

6.2.2 Sub soil

As in the top soil layer, the four Pb fractions exhibited dramatically varying concentrations, although as reflected by the lower total metal concentration the fractions displayed both narrower ranges and lower mean concentrations than the top soil layer. Again, it was noted that the exchangeable and residual fractions exhibited the lowest concentrations, substantially less than the reducible and oxidisable fractions. On average the sub soil contained almost the same proportion of oxidisable and reducible Pb. All four fractions exhibited positively skewed concentration distributions, although

as in the top soil layer, when calculated as a proportion of the total Pb, the reducible fraction exhibited a negatively skewed distribution. (Table 6.2, Figures 6.4 and 6.5).

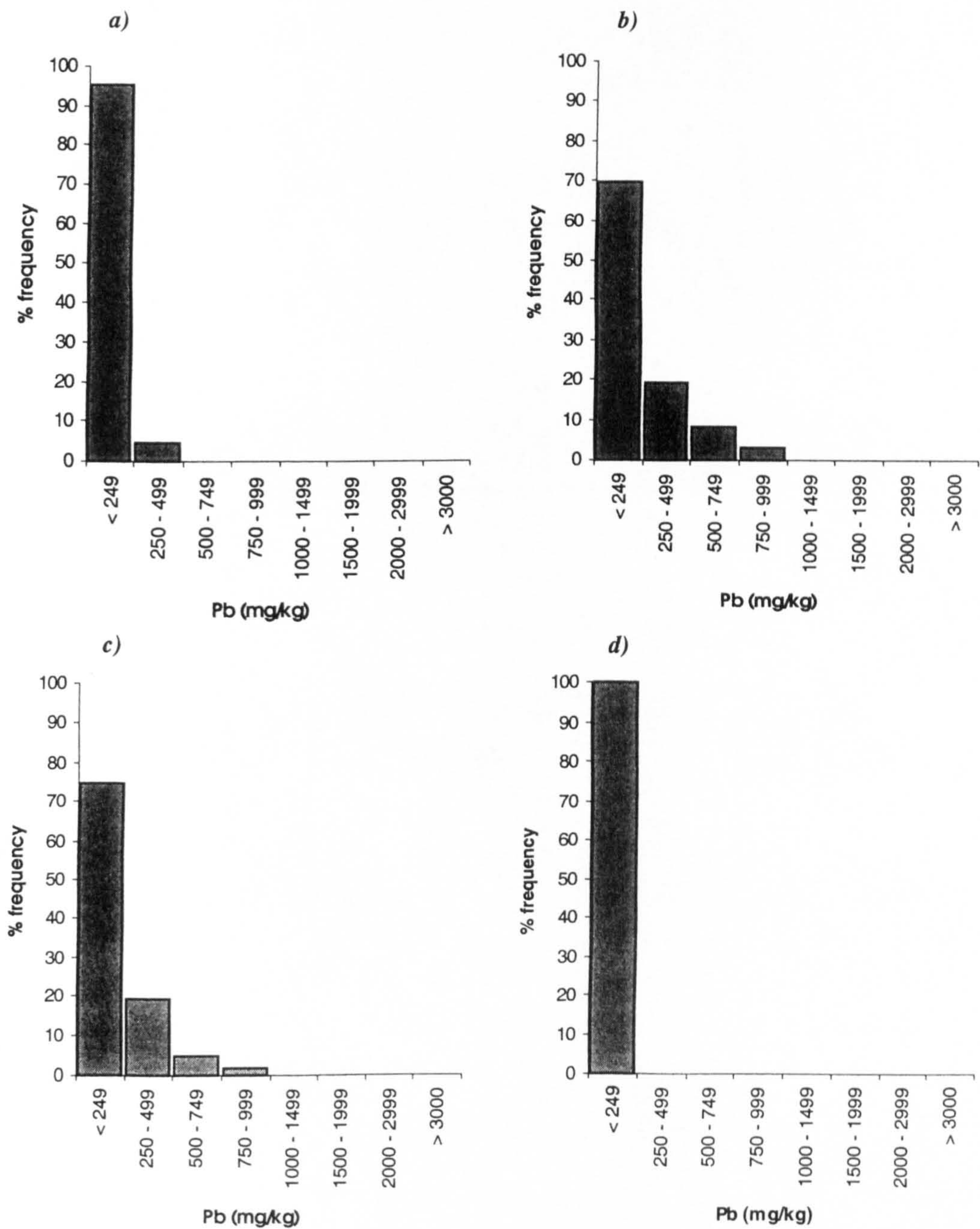


Figure 6.4 Frequency distribution of Pb fractions, sub soil (a) exchangeable; (b) reeducible; (c) oxidisable; (d) residual

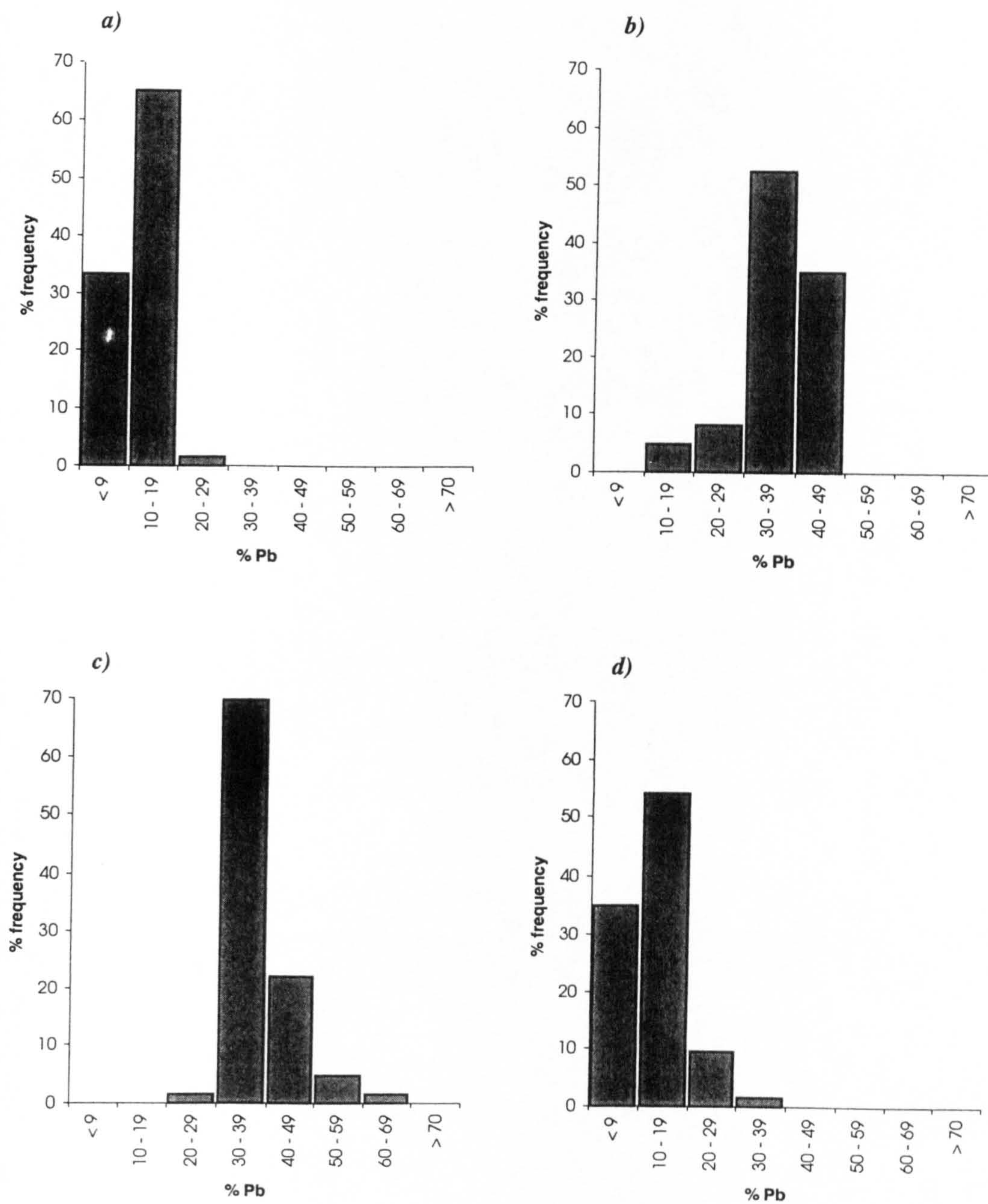


Figure 6.5 Pb partitioning, sub soil (a) exchangeable; (b) reeducible; (c) oxidisable; (d) residual

	Pb	exchangeable	reducible	oxidisable	residual	sum
Concentration (mg/kg)	mean	72	221	203	57	553
	median	46	151	164	50	404
	s.d.	75	200	144	28	435
	max.	314	928	754	136	1999
	min.	5	8	44	15	81
	skewness	1.73	1.78	1.74	1.27	1.71
Proportion (%)	mean	11.2	37.1	38.6	13.1	-
	median	11.0	38.5	38.2	11.7	-
	s.d.	4.3	7.9	6.4	5.8	-
	max.	20.5	46.9	61.0	35.9	-
	min.	2.0	10.2	29.7	4.8	-
	skewness	0.02	-1.71	1.23	1.42	-

Table 6.2 Plot I summary statistics, sub soil Pb

The spatial distribution of the exchangeable, reducible and oxidisable fractions appeared to be hot spot in nature, although pixel map classification of the Pb concentrations failed to indicate any spatial variation within the residual fraction. The reducible and oxidisable forms displayed a very similar spatial pattern, reflecting that of the total metal (Figures 6.6 and 5.8). Those samples identified as displaying higher exchangeable Pb concentrations also exhibited higher reducible and oxidisable Pb concentrations.

It was noted that within the top and sub soil layers Pb was distributed in different proportions between the four fractions. Proportionately, the top soil contained 0.65 : 3.68 : 4.64 : 1.03 of exchangeable : reducible : oxidisable : residual Pb and the sub soil contained 1.12 : 3.71 : 3.86 : 1.31. The sub soil contained a higher proportion of exchangeable and residual Pb whereas the top soil contained a higher proportion of oxidisable Pb. Both layers contained a similar proportion of the reducible fraction (Figure 6.7). A χ^2 test confirmed that there was no significant difference between the top and sub soil fractionation.

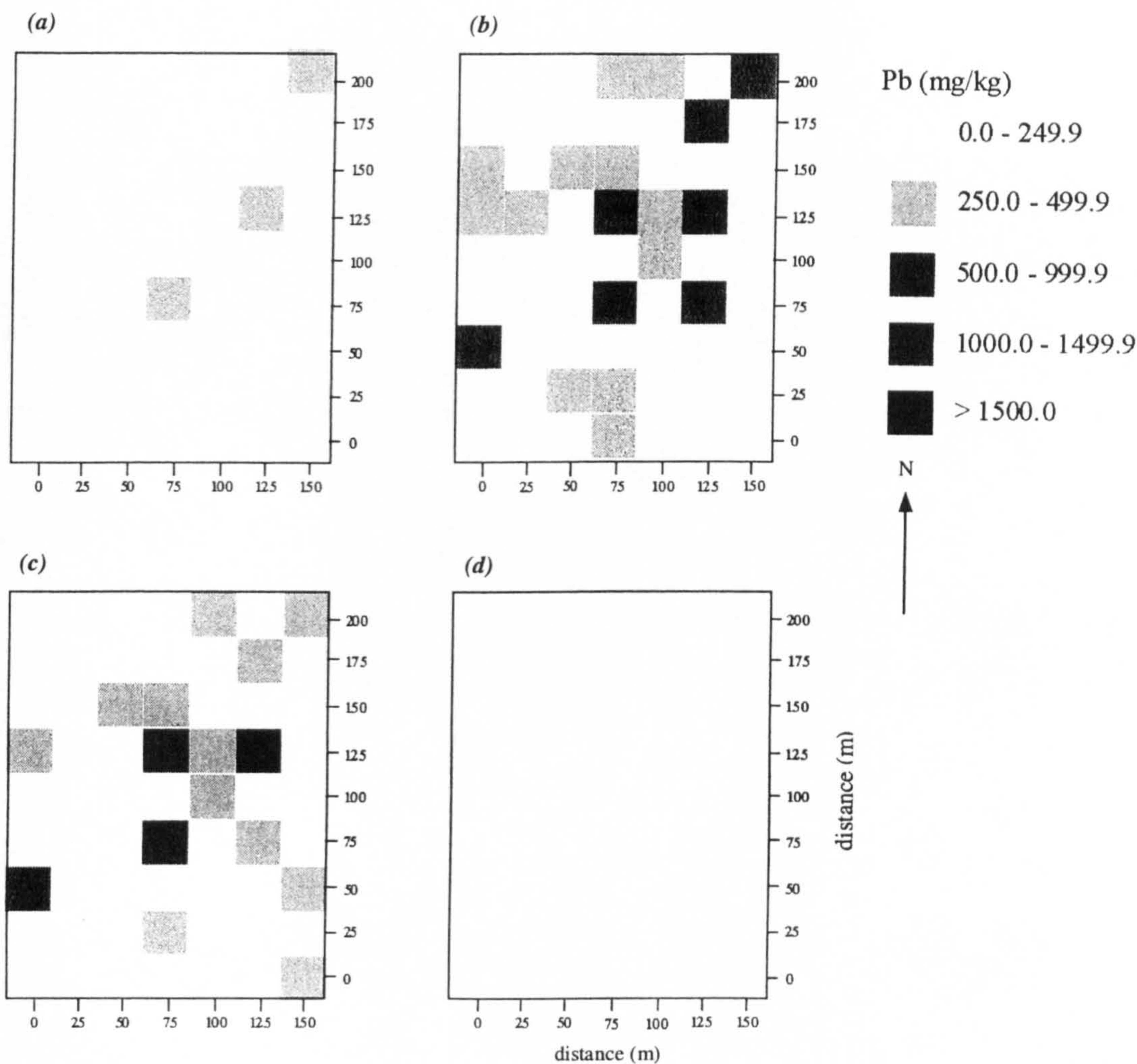


Figure 6.6 Spatial distribution, Plot I sub soil Pb fractions (a) exchangeable; (b) reducible, (c) oxidisable, (d) residual

6.3 Zn FRACTIONATION

Sequential extraction also determined that the soil of plot I contained variable concentrations of the four different forms of Zn. The fractions summed to approximately 75% of the total Zn concentration (Appendix 3), some of the metal being lost during the extraction process. Partitioning, concentration and spatial variation were again examined, for both top and sub soil layers, using means, medians, ranges and measures of skewness in addition to frequency distributions and concentration plots

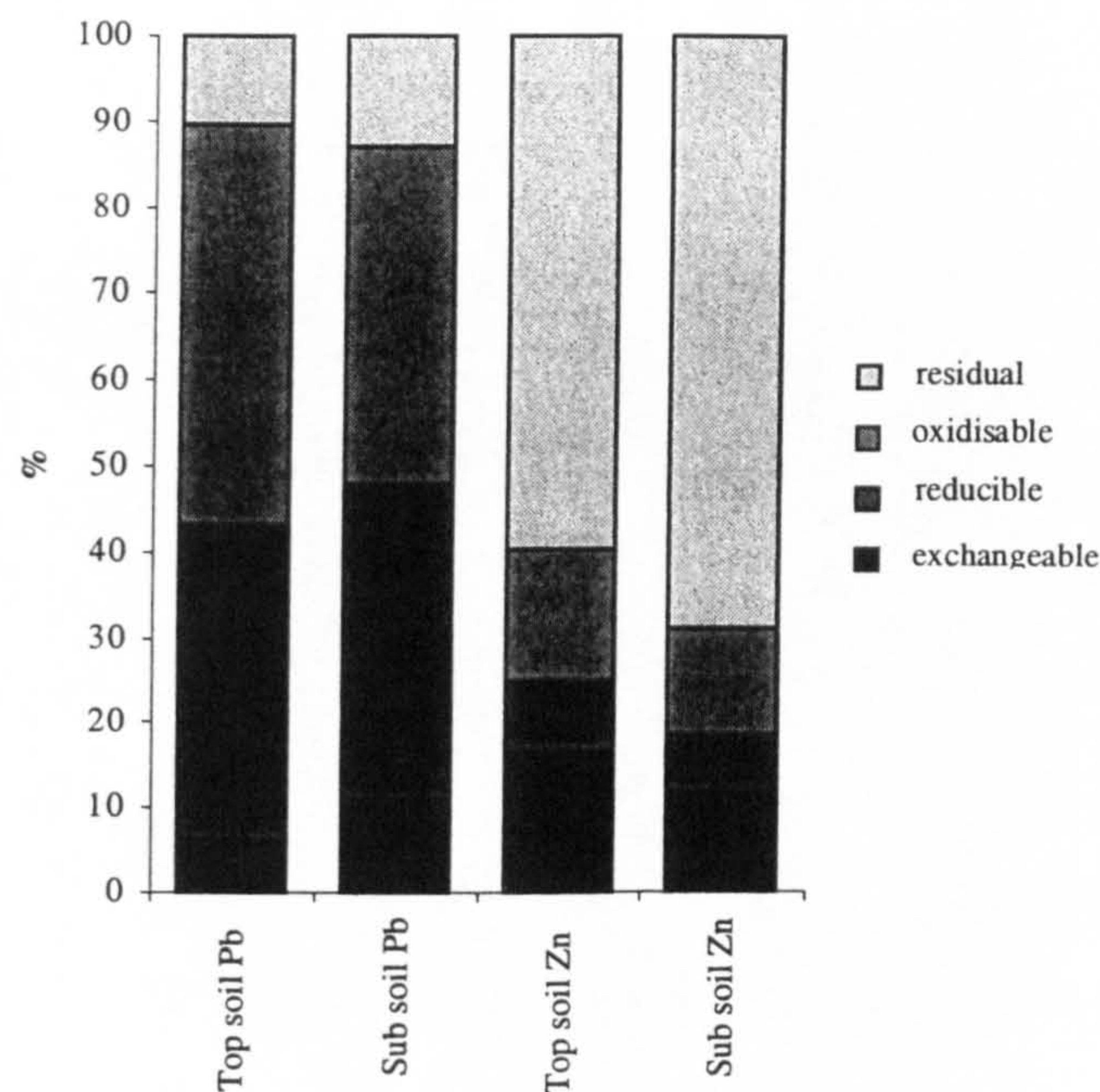


Figure 6.7 Partioning of metals (Pb and Zn) within the top and sub soil

6.3.1 Top soil

The four top soil Zn fractions exhibited variable concentrations, although as total Zn concentrations were relatively low, ranges were notably narrower than for Pb. The residual Zn fraction exhibited the highest mean concentration, approximately 4 times greater than the exchangeable and oxidisable fractions. The reducible fraction formed the smallest proportion of the total metal. On average nearly 60% of the top soil total Zn was of the least available, residual form. The most readily available, exchangeable fraction constituted approximately 17% of the total metal, a notably higher proportion than the exchangeable Pb fraction. All four fractions exhibited positively skewed concentration distributions (Table 6.3, Figures 6.8 and 6.9).

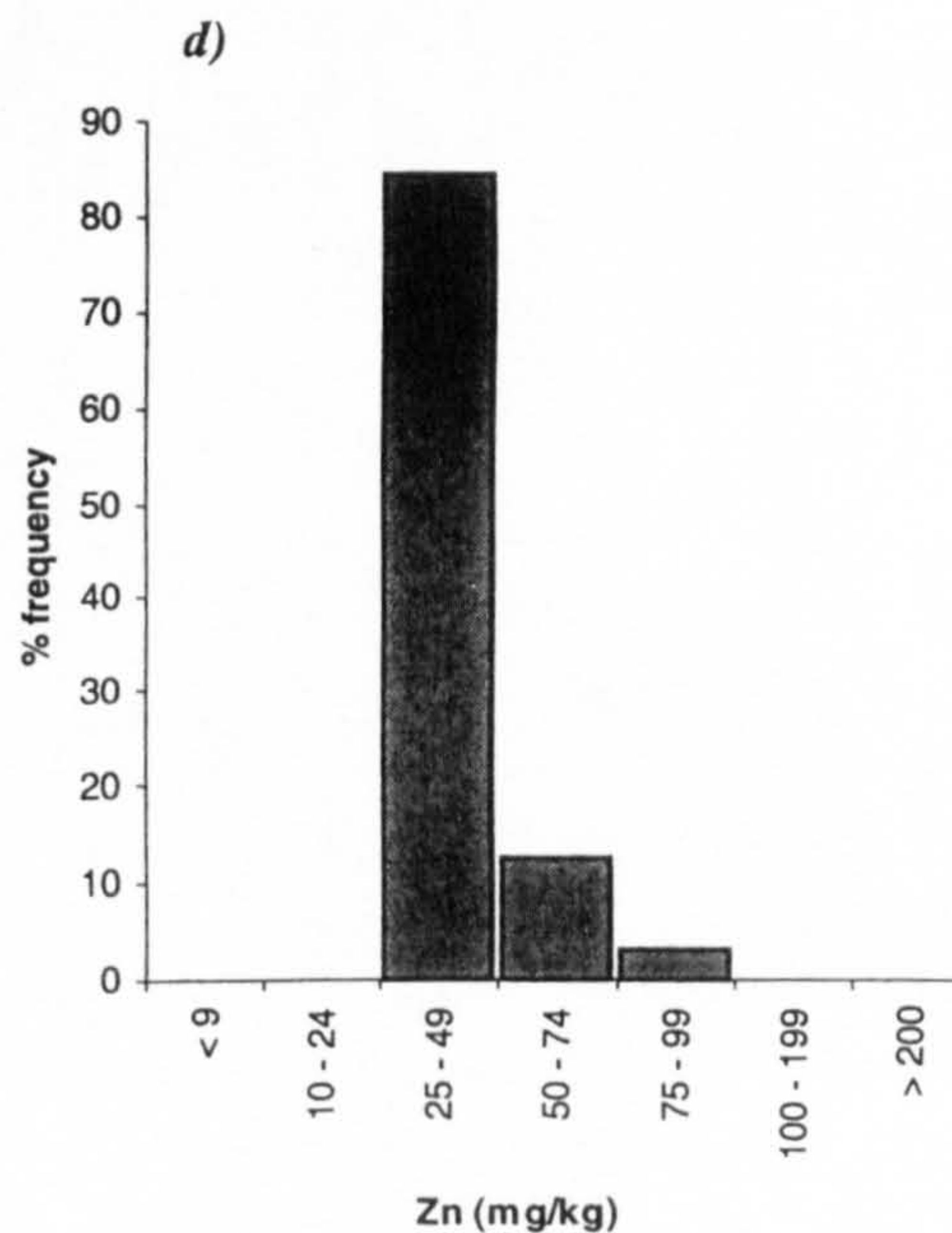
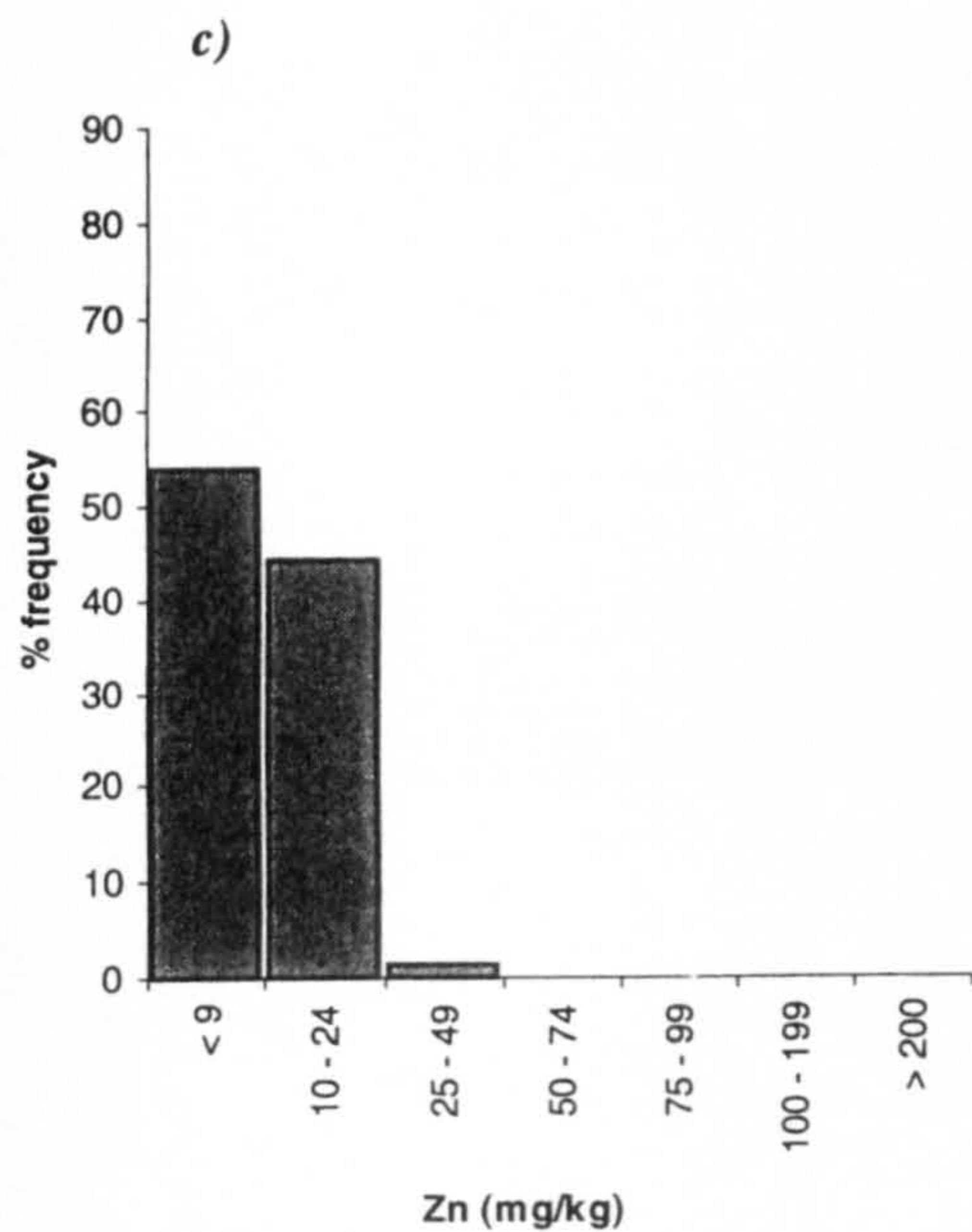
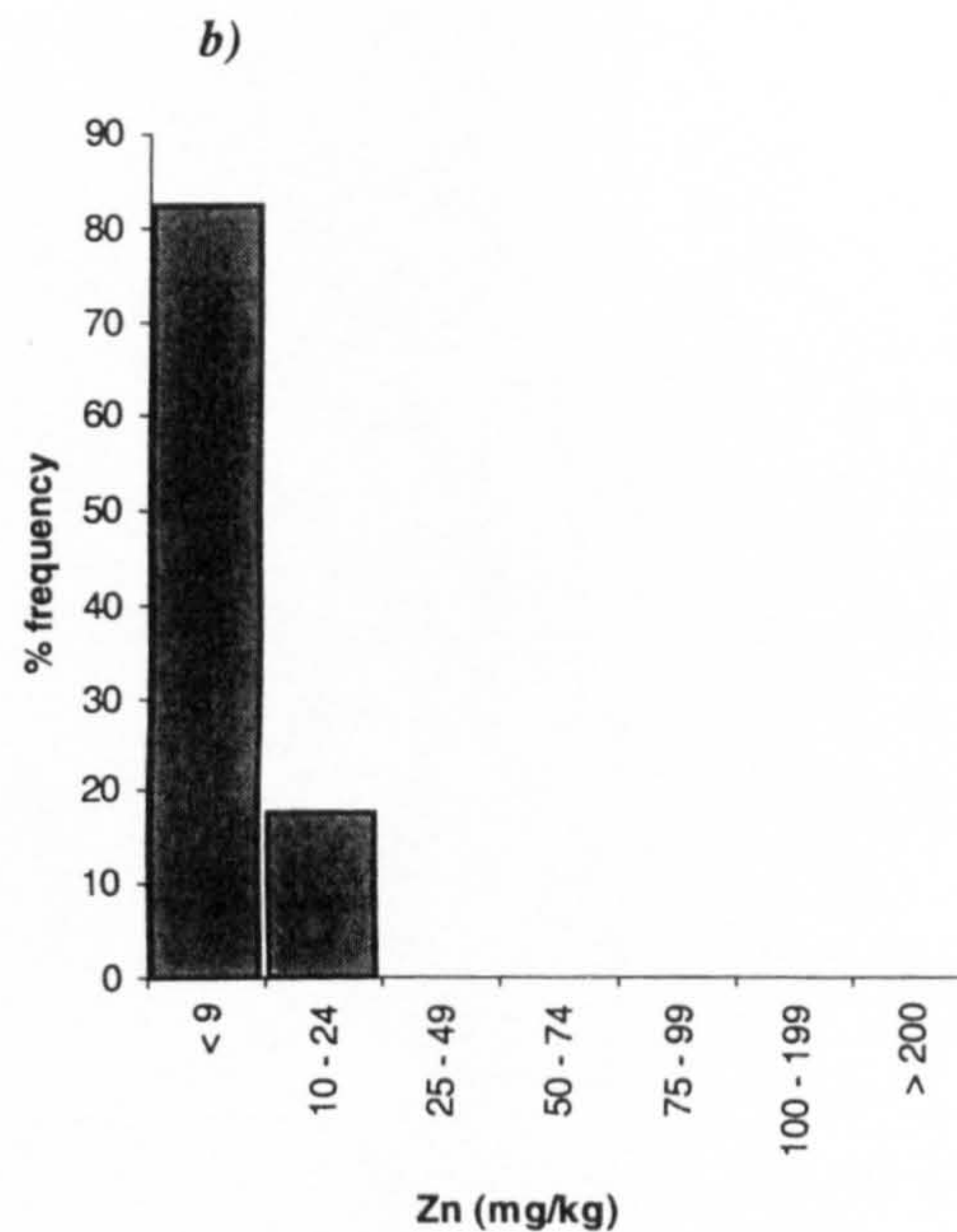
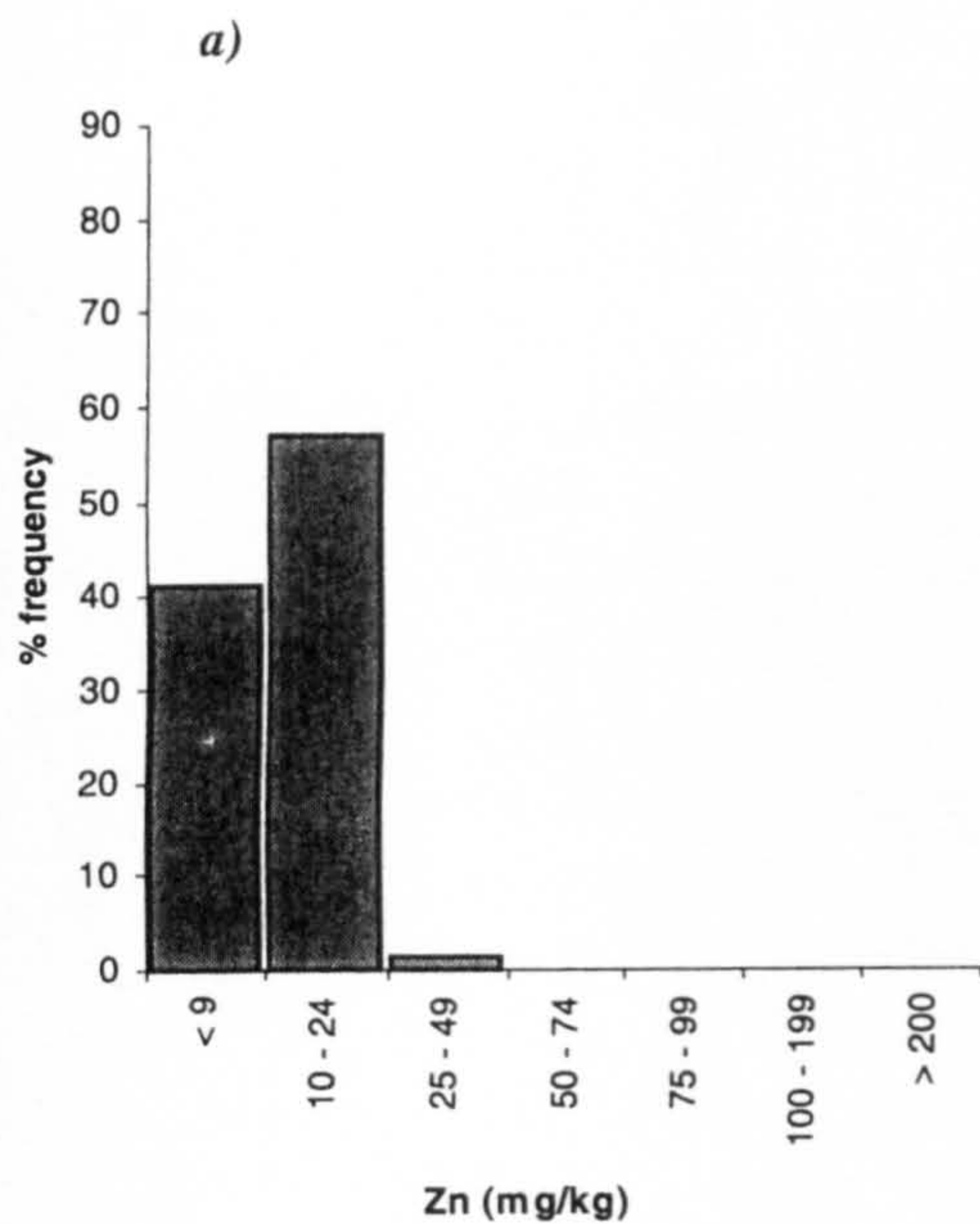


Figure 6.8 Frequency distribution of Zn fractions, top soil (*a*) exchangeable; (*b*) reeducible; (*c*) oxidisable; (*d*) residual

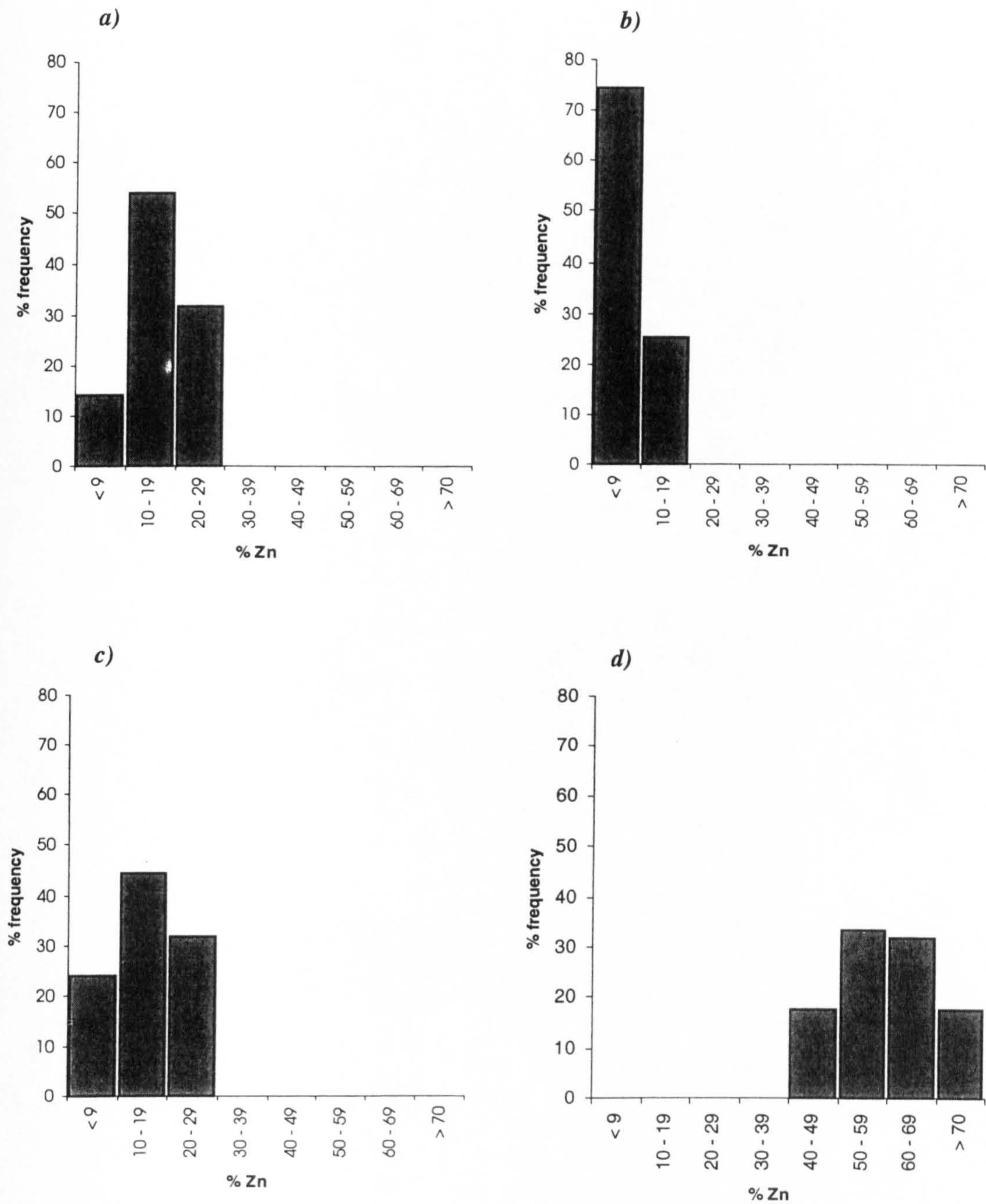


Figure 6.9 Zn partitioning, top soil (a) exchangeable; (b) reeducible; (c) oxidisable; (d) residual

Zn		exchangeable	reducible	oxidisable	residual	sum
Concentration (mg/kg)	mean	12.7	6.2	11.2	42.9	73.0
	median	12.3	5.6	9.0	41.6	71.8
	s.d.	6.0	3.4	5.8	11.9	18.9
	max.	25.9	16.2	28.9	95.7	147.3
	min.	2.1	0.8	3.7	26.2	41.0
	skewness	0.21	0.74	0.80	2.55	1.20
Proportional (%)	6.9	12.4	68.8	15.2	59.6	-
	5.7	12.6	69.5	12.6	59.8	-
	3.7	3.2	5.8	6.6	9.5	-
	15.3	21.4	79.7	27.1	78.5	-
	1.1	4.6	47.7	5.7	40.8	-
	0.60	0.00	-1.03	0.47	0.05	-

Table 6.3 Plot I summary statistics, top soil Zn

The four Zn fractions exhibited variable patterns of spatial distribution, which also differed from the total metal (Figures 6.10 and 5.10). In general, the western side of the plot exhibited higher concentrations of exchangeable and oxidisable Zn, although the highest concentrations of residual Zn were mainly within the north and south. The reducible fraction exhibited a hot spot pattern of distribution, with samples displaying higher concentrations often isolated and surrounded by others of lower concentration (Figure 6.10).

6.3.2 Sub soil

The sub soil Zn fractions exhibited similar concentration ranges to the top soil fractions, with the residual fraction displaying both the widest range and the highest mean concentration. As in the top soil, the reducible fraction constituted the lowest and the residual fraction the greatest proportion of the total Zn. Within the sub soil layer almost 70% of the Zn was of the residual form. Compared to the top soil a lower proportion of sub total Zn was in the exchangeable, most readily available form. All four fractions exhibited positively skewed concentration distributions (Table 6.4, Figures 6.11 and 6.12).

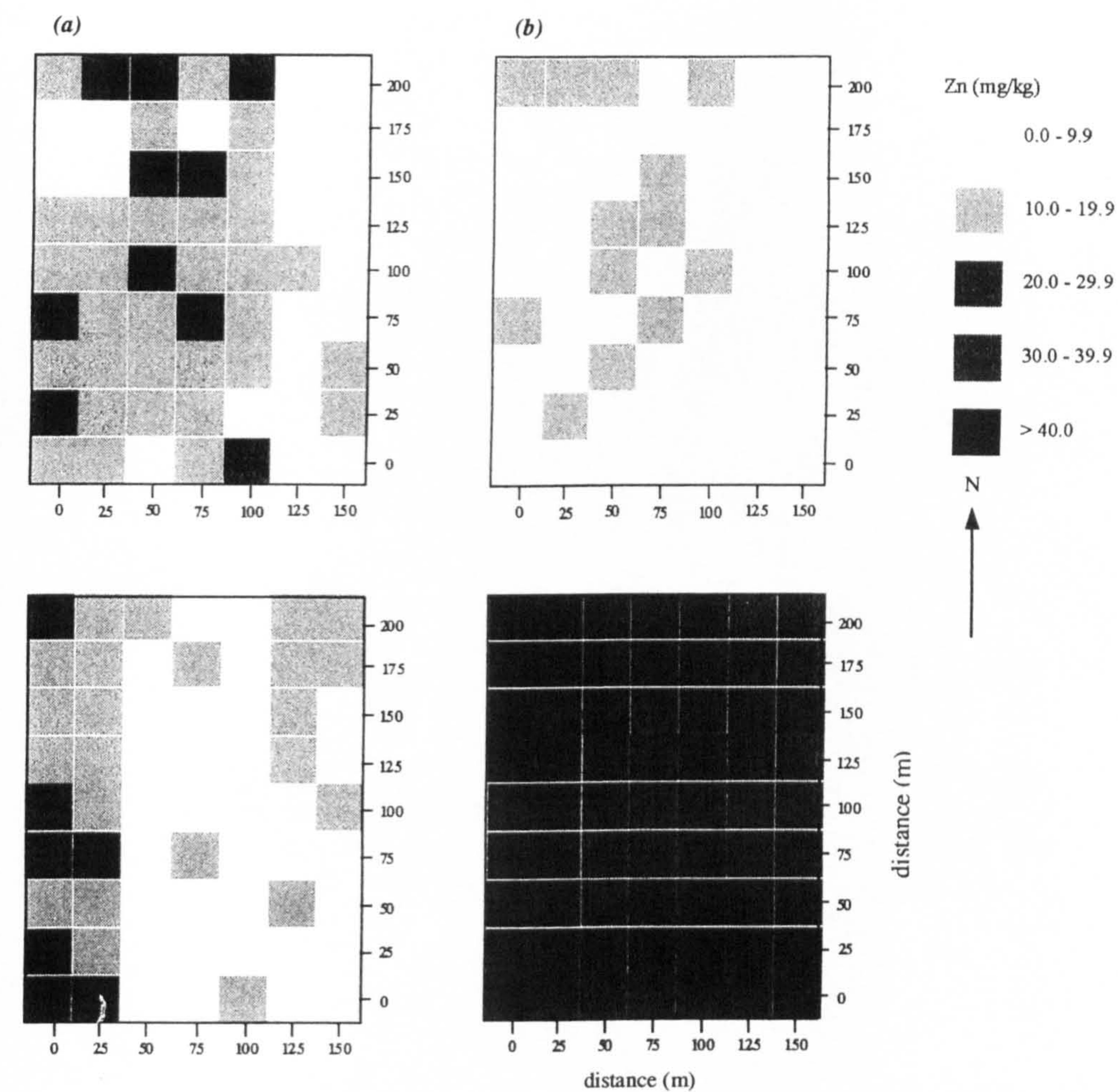


Figure 6.10 Spatial distribution, Plot I top soil Zn fractions (a) exchangeable; (b) reducible, (c) oxidisable, (d) residual

Zn		exchangeable	reducible	oxidisable	residual	sum
Concentration (mg/kg)	mean	6.3	3.9	6.8	37.1	54.1
	median	5.6	2.9	6.4	35.6	53.2
	s.d.	3.2	2.4	3.2	8.6	13.3
	max.	25.0	12.6	23.6	80.9	130.4
	min.	3.2	0.4	2.1	23.8	36.5
	skewness	3.88	0.93	3.30	2.64	3.59
Proportion (%)	mean	11.8	6.9	12.4	68.8	-
	median	10.8	5.7	12.6	69.5	-
	s.d.	5.3	3.7	3.2	5.8	-
	max.	41.9	15.3	21.4	79.7	-
	min.	5.2	1.1	4.6	47.7	-
	skewness	3.81	0.60	0.00	-1.03	-

Table 6.4 Plot I summary statistics, sub soil Zn

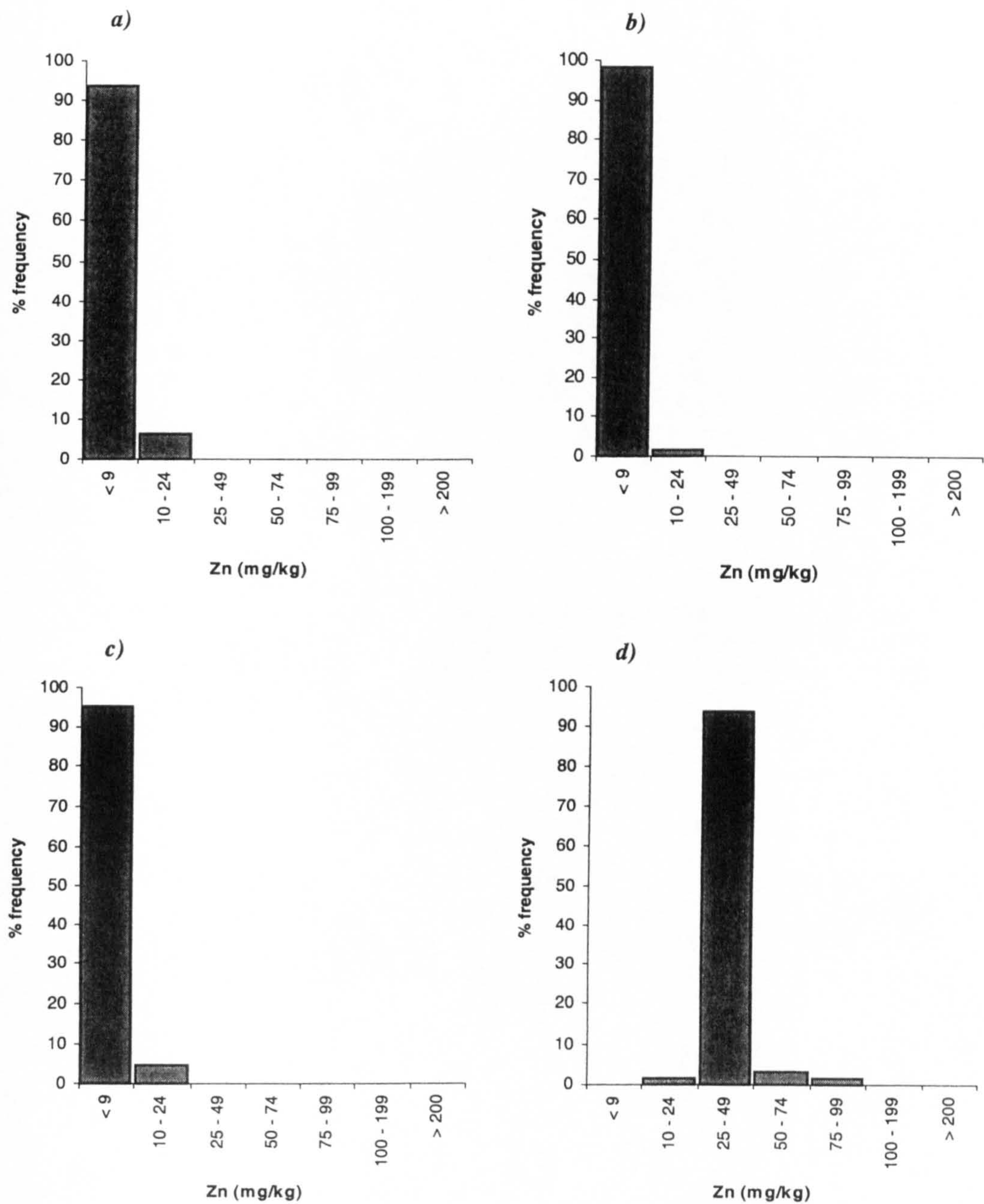


Figure 6.11 Frequency distribution of Zn fractions, sub soil (a) exchangeable; (b) reeducible; (c) oxidisable; (d) residual

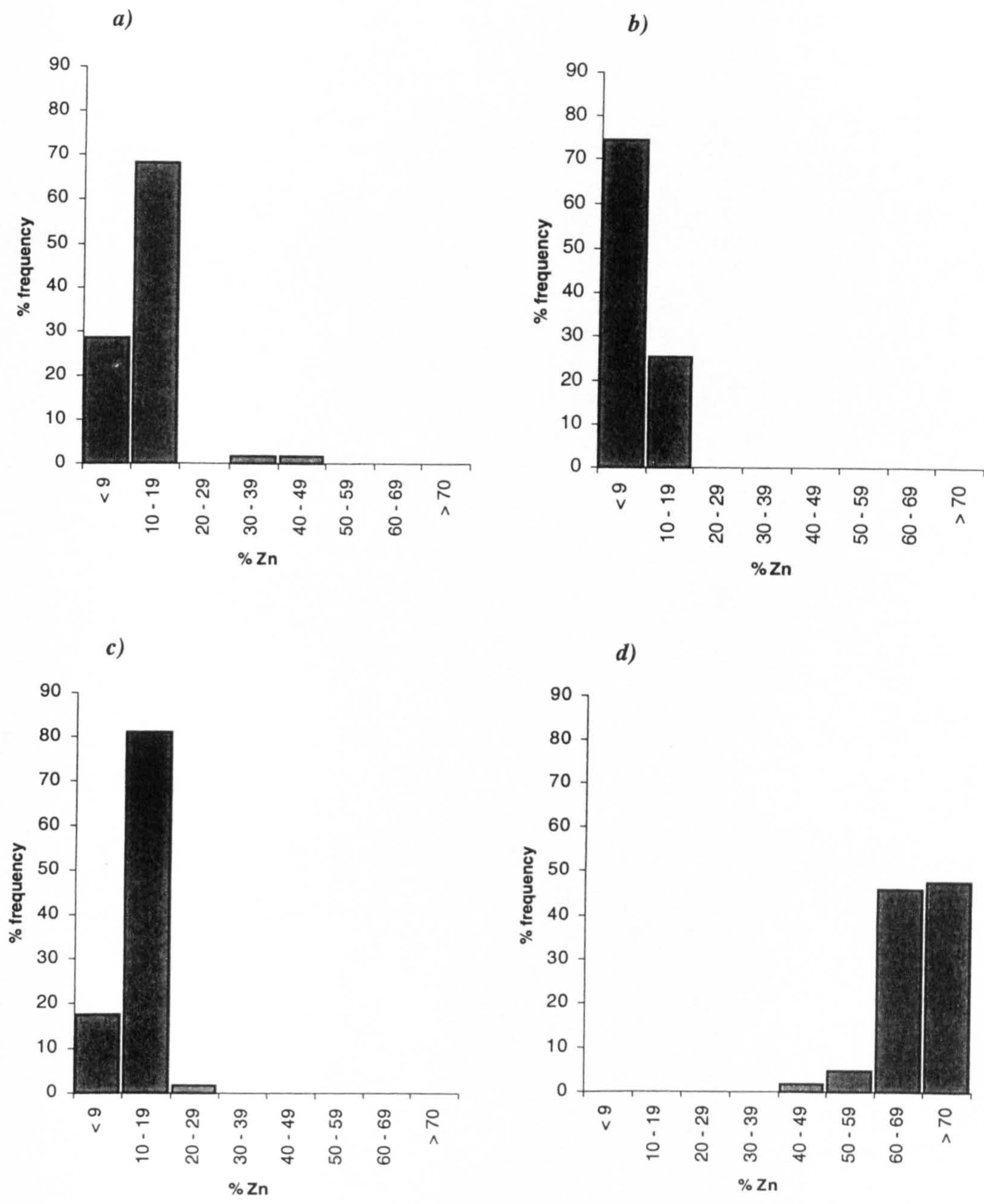


Figure 6.12 Zn partitioning, sub soil (a) exchangeable; (b) reeducible; (c) oxidisable; (d) residual

The exchangeable, reducible and oxidisable Zn fractions exhibited little spatial variation, with any variation being both simpler and less marked than within the top soil layer (Figures 6.13 and 5.10). Spatial variation was in the form of isolated samples,

with samples displaying high concentrations often adjacent to others of low concentration. The residual fraction on the other hand displayed a more complex pattern of spatial distribution. In line with the top soil layer, samples containing the highest concentrations of residual Zn were located towards the north or south of the plot. In general locations exhibiting > 40mg/kg of sub soil residual Zn also exhibited > 40mg/kg of top soil residual Zn (Figure 6.13).

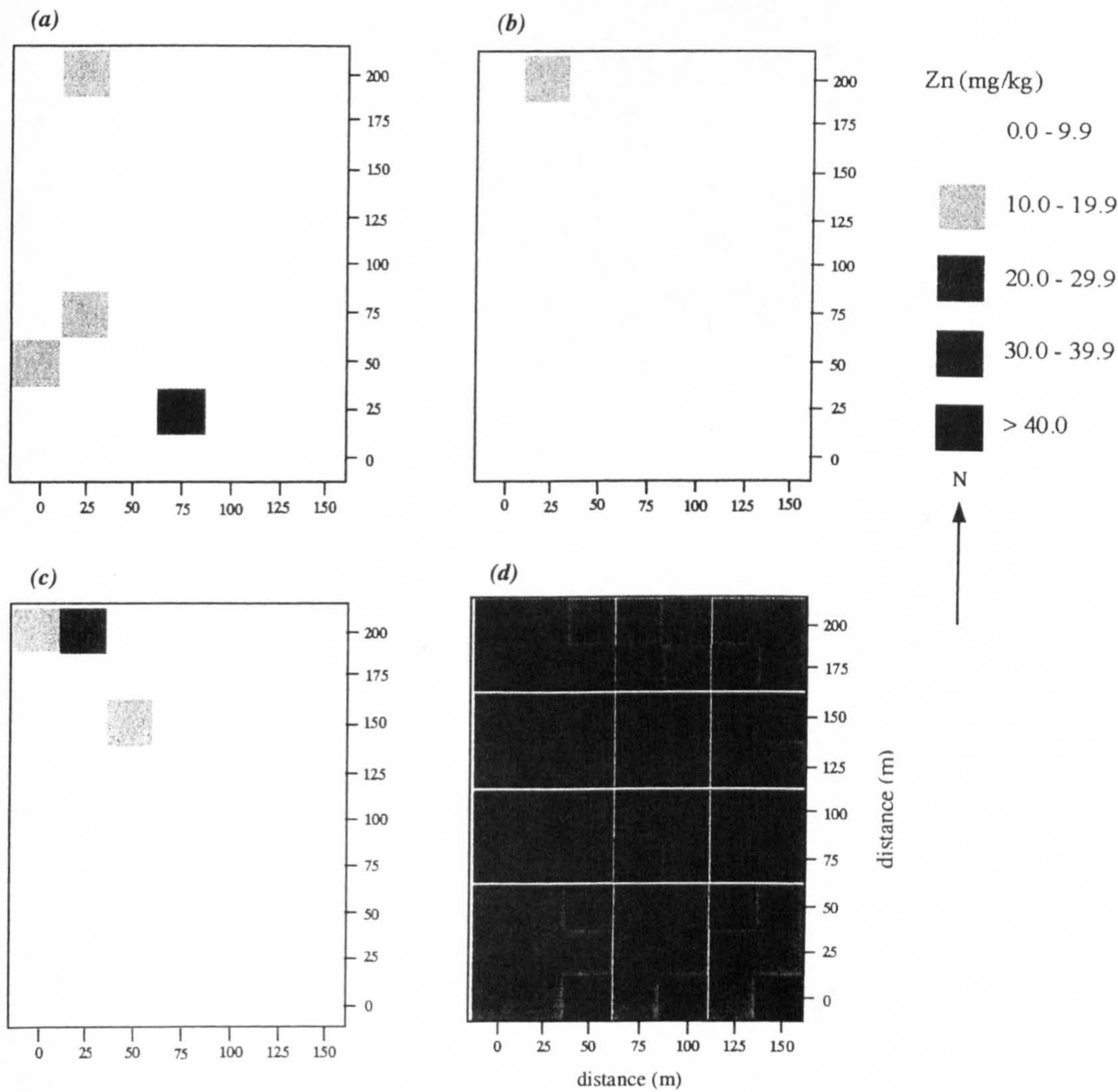


Figure 6.13 Spatial distribution, Plot I sub soil Zn fractions (a) exchangeable; (b) reducible, (c) oxidisable, (d) residual

It was noted that within the top and sub soil layers the majority of Zn was in the residual form. Proportionately, the top soil contained 1.69 : 0.82 : 1.52 : 5.98 of exchangeable : reducible : oxidisable : residual Zn and the sub soil layer 1.18 : 0.69 : 1.24 : 6.95. The reducible and oxidisable fractions constituted similar proportions of Zn, although the exchangeable and residual fractions differed. The top soil layer contained 6.5% more exchangeable Zn than the sub soil layer, whereas the sub soil layer contained 9.7% more residual Zn (Figure 6.7). A χ^2 test confirmed that there was no significant difference in Zn fractionation within the two soil layers. The bulk of the total Pb (approximately 80%) was evenly split between the reducible and oxidisable fractions, with only about 10% in the residual form. In contrast, much of the total Zn (approximately 60%) was found to be of the residual form, and the proportion of exchangeable Zn was slightly higher than that of exchangeable Pb (Figure 6.7). A χ^2 test determined that the differences in partitioning between Pb and Zn were not statistically significant.

6.4 SPATIAL DEPENDENCE

This section describes, using omni-directional variograms, the spatial dependence of the four Pb and Zn fractions within the top and sub soil of plot I. The variograms have been modelled using the method of least squares and the parameters, range, sill variance, nugget variance and slope, used to assess the relationships between samples (Appendix 5). In addition to examining the top and sub soil individually, data from the two soil layers have been combined assessing the effect of doubling the number of samples on the resultant variograms.

Optimised variogram parameters, lag spacing and lag tolerance, were identical to those determined for total Pb and Zn within plot I (Section 5.3), 25m and 12.5m, respectively (Table 5.7). Again, due to the small number of samples collected the rules of Journé and Huijbregts (1978) were not strictly adhered to with extra lags, exceeding the maximum distance of reliability, examined before variogram modelling. Outliers were removed prior to analysis with those data sets still exhibiting coefficients of skewness in

excess of $|1.0| \log_{10}$ transformed. Too few samples were available to allow analysis to proceed beyond the production of omni-directional variograms.

6.4.1 Pb fractions

Within both soil layers, the four Pb fractions exhibited variograms that could be best modelled by linear functions, revealing similarities in their geographical configuration (Figures 6.14 and 6.15). The absence of variogram sills indicated that, over the distance for which variograms had been calculated, soil Pb concentrations remained dependent upon each other. The same general characteristics were exhibited by variograms computed from the combined top and sub soil data (Figure 6.16).

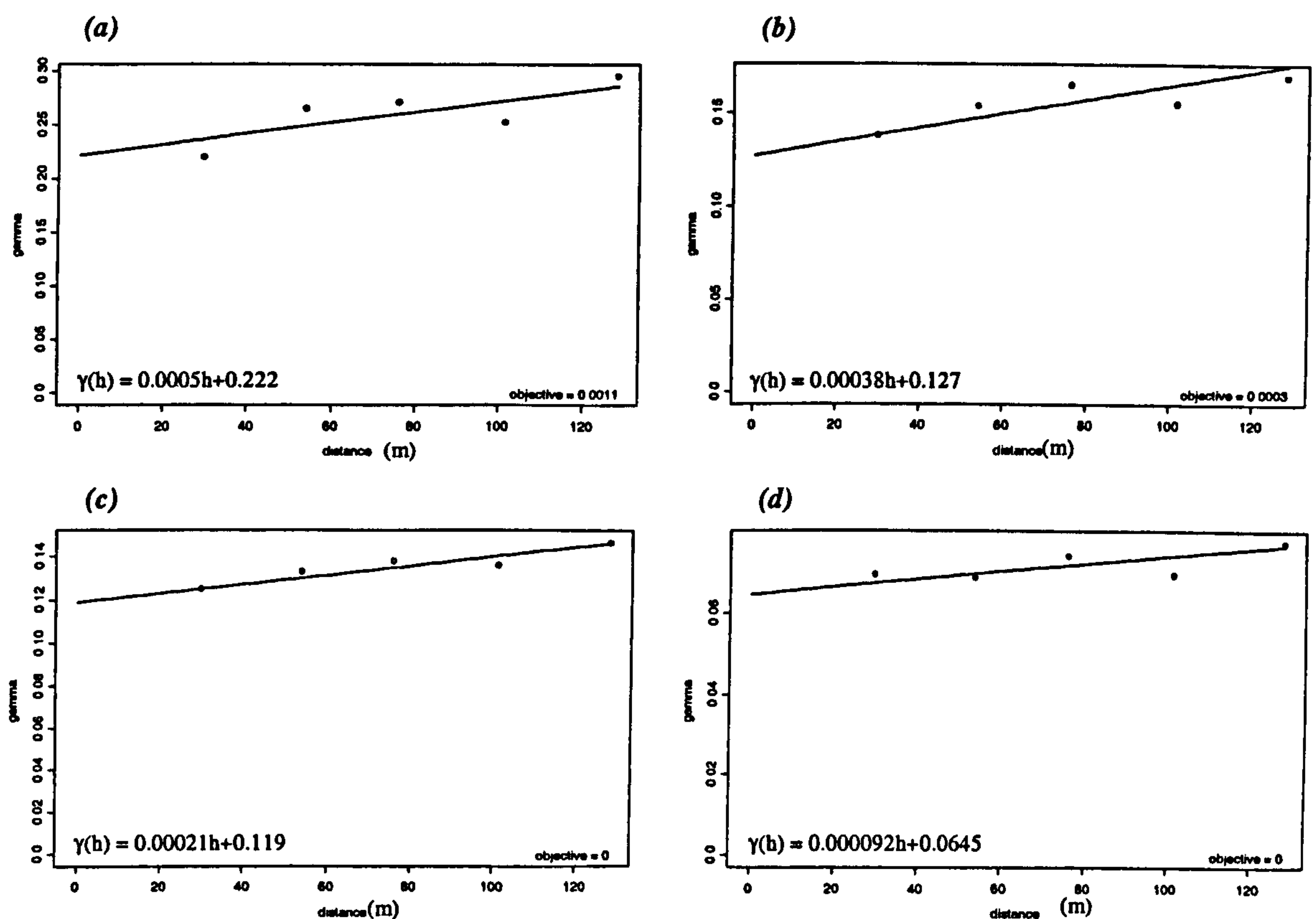


Figure 6.14 Omni-directional variograms, plot I top soil (a) exchangeable Pb, (b) reducible Pb, (c) oxidisable Pb, (d) residual Pb

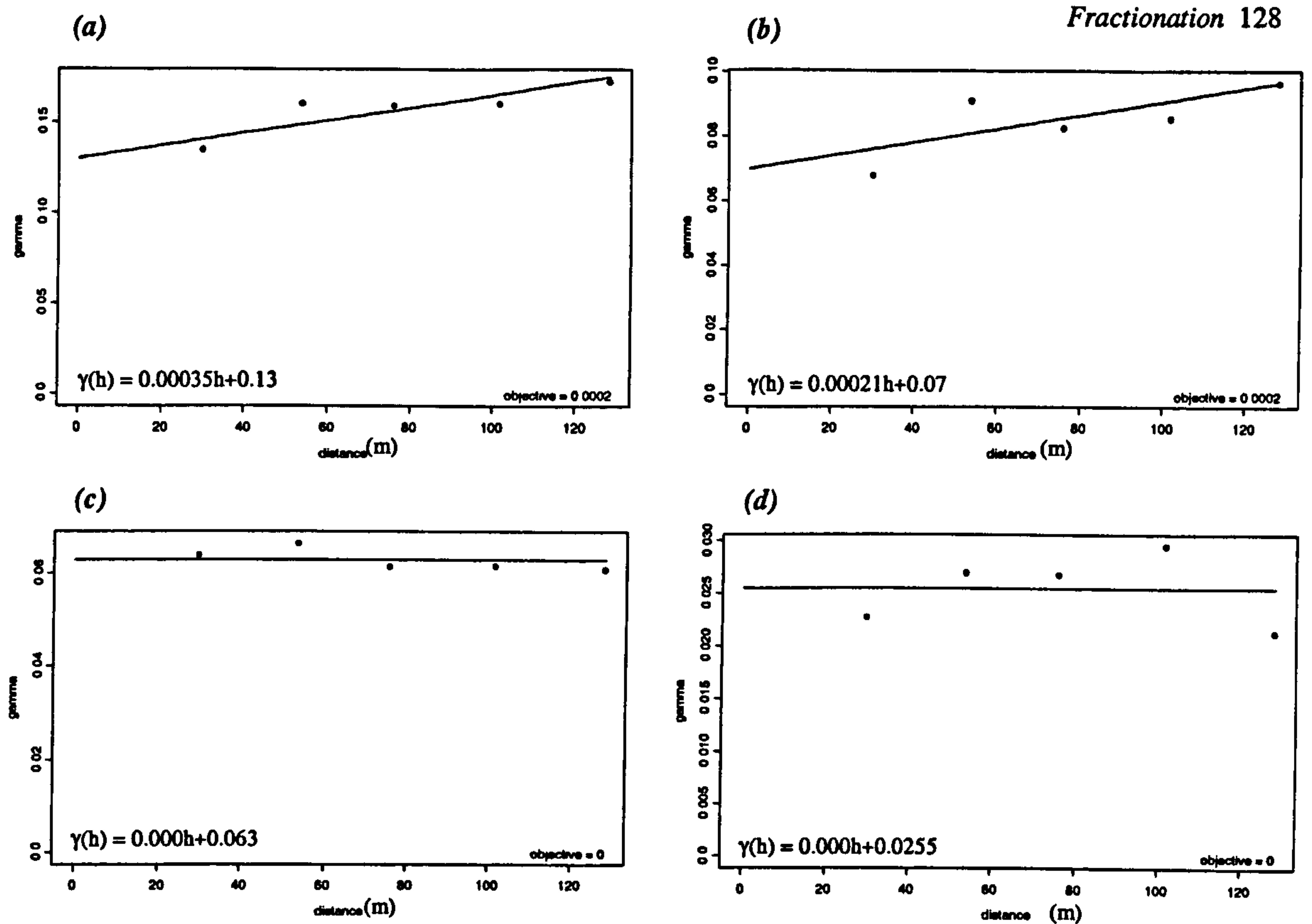


Figure 6.15 Omni-directional variograms, plot I sub soil (a) exchangeable Pb, (b) reducible Pb, (c) oxidizable Pb, (d) residual Pb

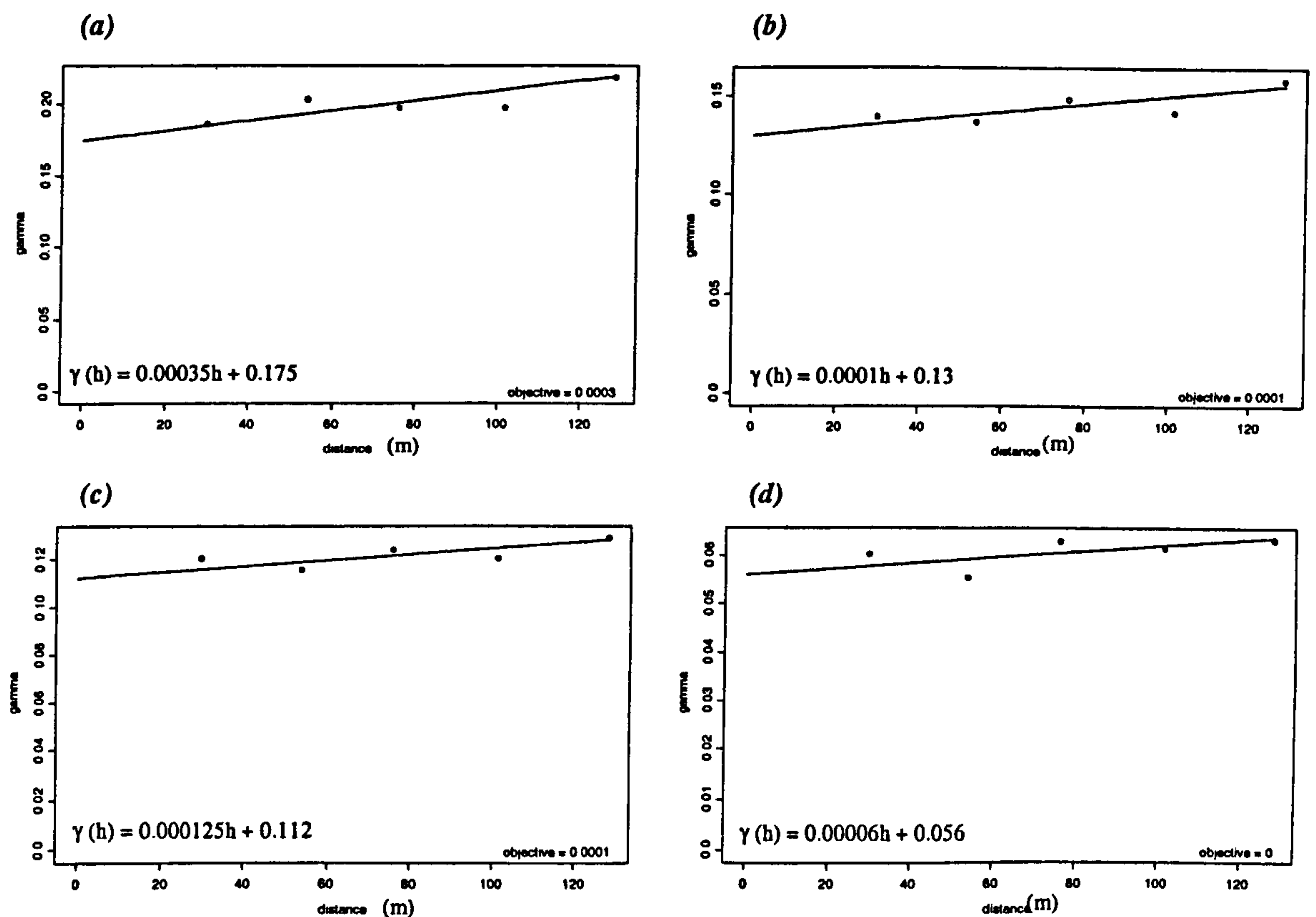


Figure 6.16 Omni-directional variograms, plot I combined top and sub soil (a) exchangeable Pb, (b) reducible Pb, (c) oxidizable Pb, (d) residual Pb

Substantial differences were noted in the slopes of the variograms indicating that certain Pb fractions were more spatially dependent than others (Table 6.5). In general, the top soil exhibited steeper variograms than the sub soil, although a similar strength order of dependence was noted within both soil layers. The same order was identified when data from the top and sub soil was combined. The exchangeable and reducible fractions exhibited the strongest spatial dependence, thought possibly to reflect their potential mobility and availability within the soil. The lowest spatial dependence was displayed by the residual, potentially unavailable fraction. It was noted that variograms computed for the combined data exhibited gradients between those of the individual top and sub soil layers.

	fraction	model	range (m)	sill variance (m)	slope	nugget variance (γ)
top soil	exchangeable	linear	-	-	0.00050	0.222
	reducible	linear	-	-	0.00038	0.127
	oxidisable	linear	-	-	0.00020	0.119
	residual	linear	-	-	0.000092	0.0645
sub soil	exchangeable	linear	-	-	0.00035	0.130
	reducible	linear	-	-	0.00021	0.070
	oxidisable	linear	-	-	0.000	0.063
	residual	linear	-	-	0.000	0.0255
combined	exchangeable	linear	-	-	0.00035	0.175
	reducible	linear	-	-	0.0001	0.13
	oxidisable	linear	-	-	0.000125	0.112
	residual	linear	-	-	0.00006	0.056

Table 6.5 Omni-directional variogram parameters, plot I Pb fractions

Within the sub soil, the oxidisable and residual fractions were best modelled by purely nugget variograms, indicative of either an absence of spatial structure or the occurrence of spatial dependence over a substantially shorter distance than the smallest sampling interval. The lack of spatial structure perhaps reflects the inherent stability and unavailability of these two Pb fractions within the soil. All variograms exhibited large nugget variances suggesting the occurrence of a substantial degree of variation at distances less than 25m.

6.4.2 Zn fractions

The majority of the top and sub soil Zn fractions exhibited variograms that could be best modelled by linear functions absent of variogram sills (Figures 6.17 and 6.18); these

fractions therefore displayed spatial dependence over a greater distance than the variograms had been computed. The top soil residual and sub soil reducible fractions however, exhibited bounded type variograms, best modelled by spherical functions. These two fractions were spatially dependent over distances of 91 and 110m, respectively (Table 6.6). Amalgamation of the top and sub soil data resulted in linear variograms for all four fractions (Figure 6.19). All variograms exhibited nugget variances suggesting that variation was occurring at distances less than the shortest sampling interval, 25m. A mixture of transformed and non-transformed data made comparison of variograms difficult, hence discussion will be mainly limited to the combined top and sub soil data that has been treated similarly.

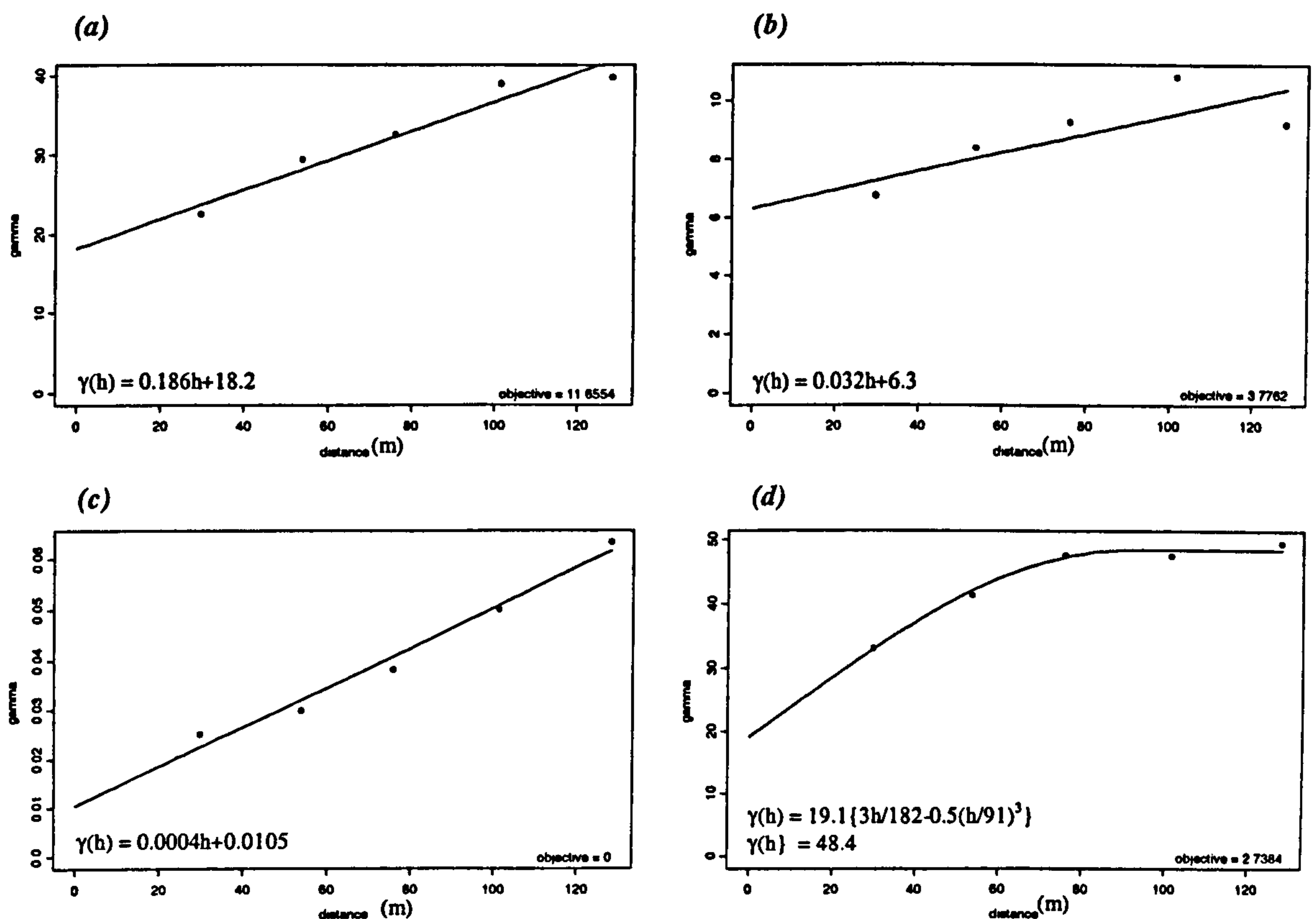


Figure 6.17 Omni-directional variograms, plot I top soil (a) exchangeable Zn, (b) reducible Zn, (c) oxidisable Zn, (d) residual Zn

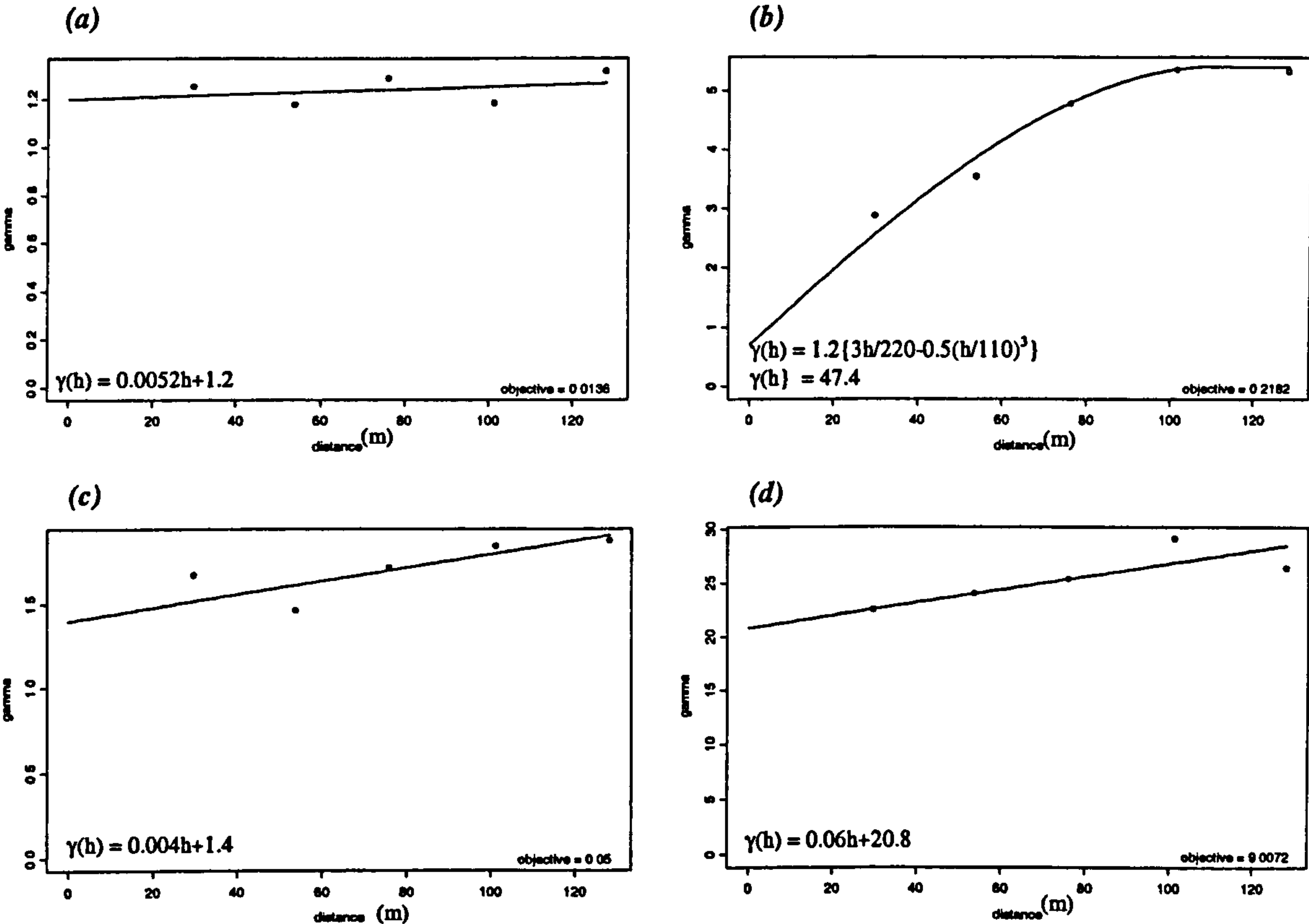


Figure 6.18 Omni-directional variograms, plot I sub soil (a) exchangeable Zn, (b) reducible Zn, (c) oxidisable Zn, (d) residual Zn

	fraction	model	range (m)	sill variance (m)	slope	nugget variance (γ)
top soil	exchangeable	linear	-	-	0.168	18.2
	reducible	linear	-	-	0.032	6.3
	oxidisable	linear	-	-	0.0004	0.0105
	residual	spherical	91	29.3	-	19.1
sub soil	exchangeable	linear	-	-	0.0052	1.2
	reducible	spherical	110	47.0	-	0.7
	oxidisable	linear	-	-	0.004	1.4
	residual	linear	-	-	0.006	20.8
combined	exchangeable	linear	-	-	0.00005	0.055
	reducible	linear	-	-	0.00008	0.065
	oxidisable	linear	-	-	0.000057	0.017
	residual	linear	-	-	0.000017	0.0046

Table 6.6 Omni-directional variogram parameters, plot I Zn fractions

The combined top and sub soil exchangeable, reducible and oxidisable Zn fractions exhibited similar levels of spatial dependence as demonstrated by their variogram slopes (Figure 6.19). The residual variogram however, was noted as displaying a gentler gradient. The differences in variogram slope are thought to reflect the relative mobility and availability of the metal fractions, the potentially unavailable residual fraction displaying the least spatial dependence. This result reflected that of the Pb fractionation. The residual variogram was also noted as displaying substantially lower semi-variances than the other three fractions, indicating a lower degree of variation. In addition, the residual variogram exhibited a smaller nugget variance than the other three fractions, hence a lower degree of spatial variation was occurring at distances less than 25m, the shortest sampling lag.

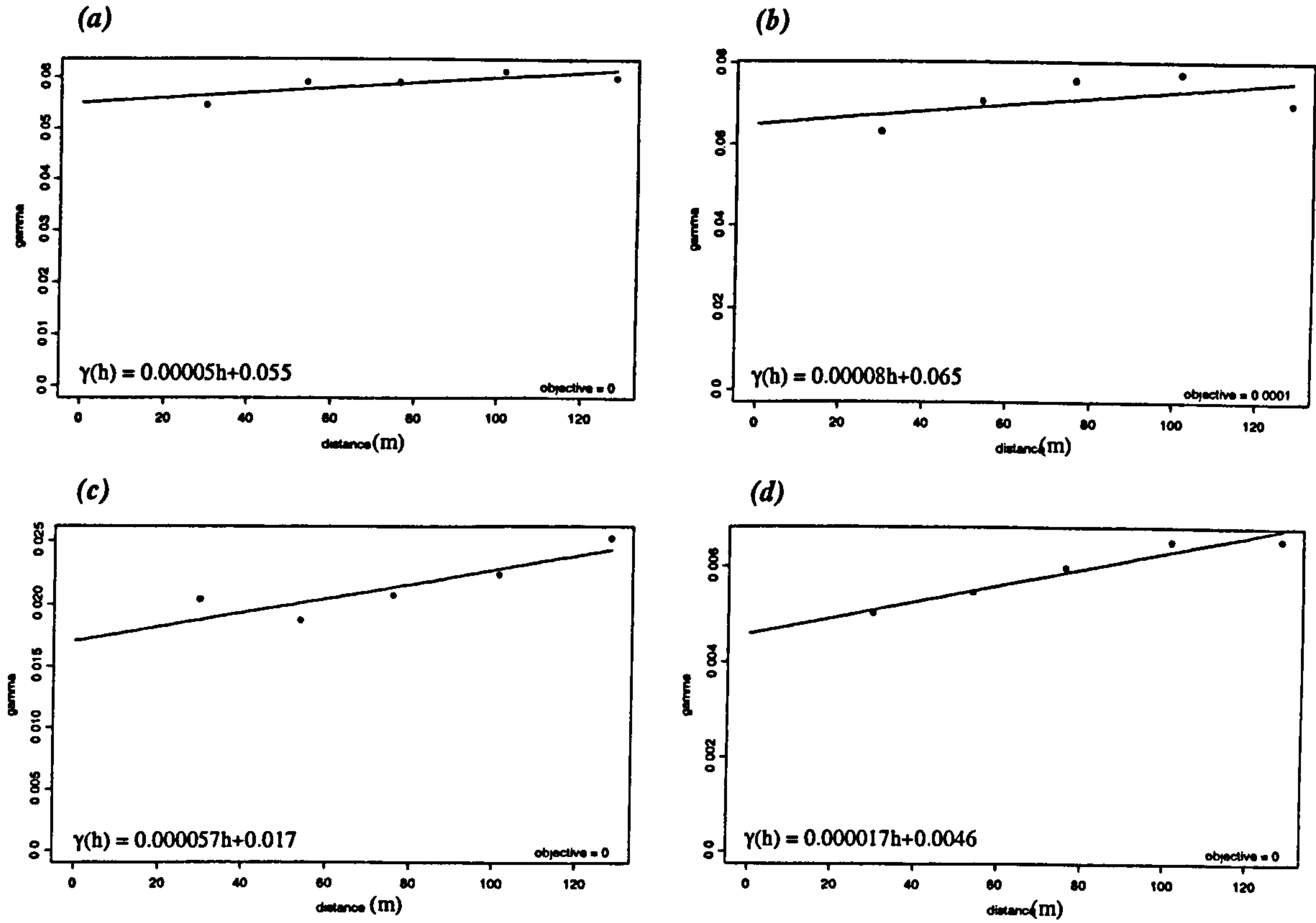


Figure 6.19 Omni-directional variograms, plot I combined top and sub soil (a) exchangeable Zn, (b) reducible Zn, (c) oxidisable Zn, (d) residual Zn

6.5 ENRICHMENT

Enrichment ratios (top soil : sub soil) provide valuable information regarding the source and potential mobility / movement of heavy metals within the soil profile. This section investigates the enrichment of Pb and Zn within the soil of plot I describing ratios for total metals in addition to the four fractions. Means, medians, ranges, coefficients of skewness and frequency distribution plots have been used to highlight variation. Spatial plots are used to indicate areas of both high and low enrichment (Section 4.5.1).

6.5.1 Pb enrichment

Total and fractional Pb concentrations displayed dramatically varying enrichment ratios (Table 6.7). In general, the ratios exceeded 1.0, i.e. top soil concentrations were higher than sub soil concentrations. The most readily available, exchangeable fraction exhibited the lowest mean top to sub soil enrichment ratio, thought possibly to reflect movement of the metal down the soil profile and/or plant uptake from the top soil. However, it was noted that the least available, residual fraction displayed a very similar mean enrichment ratio to the exchangeable fraction. The highest mean ratios were exhibited by the oxidisable and reducible fractions, of medium relative availability and mobility. The top soil contained, on average, three times more total Pb than the sub soil, indicating an anthropogenic rather than geological source of the contamination. All five data sets were positively skewed (Figures 6.20a and 6.21).

Pb	total	exchangeable	reducible	oxidisable	residual
mean	3.1	2.4	3.9	4.0	2.5
median	2.0	1.1	2.2	2.9	1.8
s.d.	2.8	3.2	5.5	3.6	1.9
max.	13.0	14.3	34.5	15.8	9.0
min.	0.6	0.2	0.6	0.7	0.4
skewness	1.82	2.31	3.90	1.73	1.48

Table 6.7 Enrichment ratios (top soil : sub soil), Pb

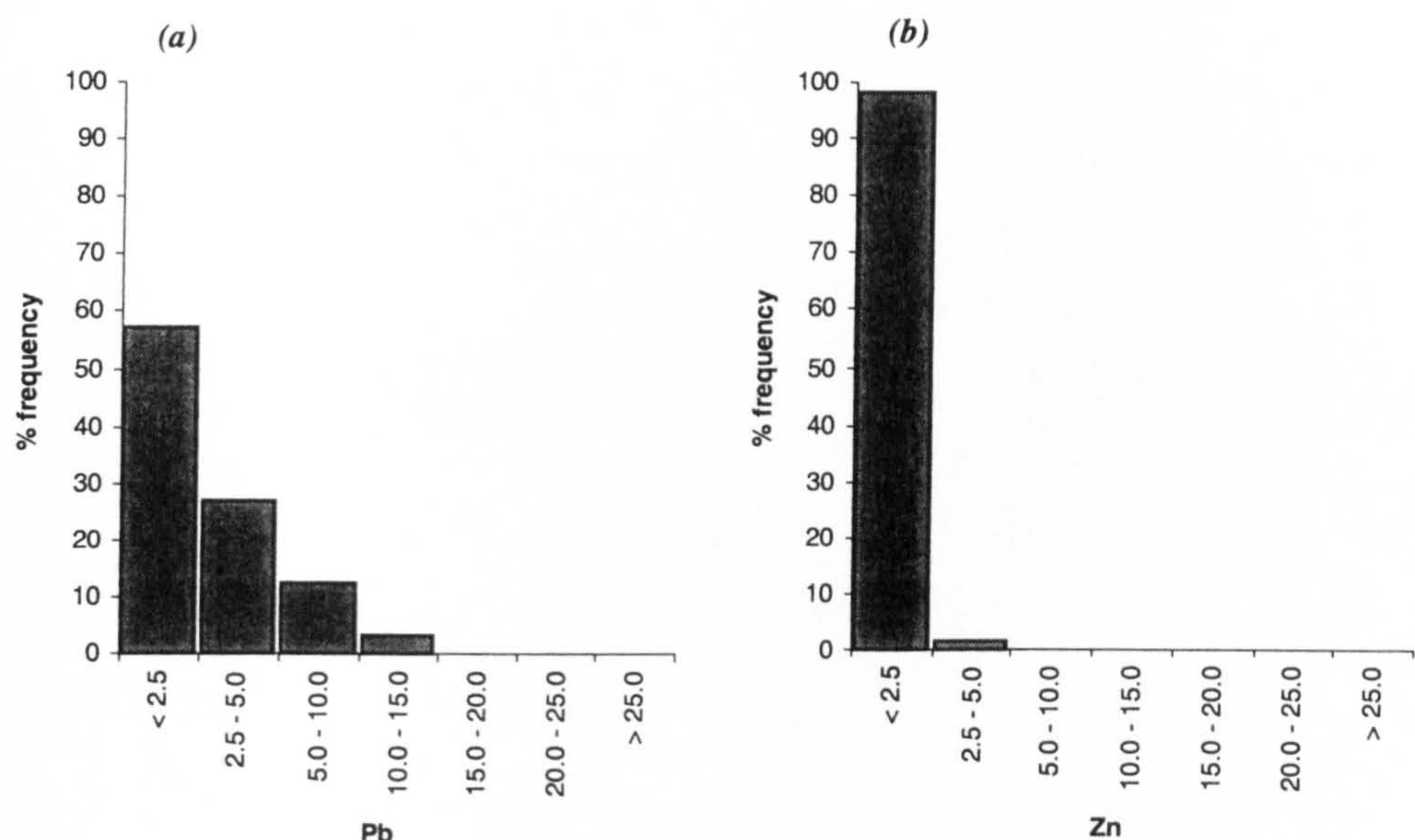


Figure 6.20 Frequency distribution of enrichment ratios (top soil : sub soil), (a) total Pb, (b) total Zn

In general, the highest enrichment ratios were scattered across the eastern side of the plot, a pattern that was particularly evident for the exchangeable and reducible fractions (Figures 6.22a and 6.23). The distribution appeared to be hot spot in nature, with individual sample points displaying higher enrichment ratios often adjacent to others exhibiting notably lower ratios. There was good general agreement between total Pb and the four fractions, with good coincidence between the sample points exhibiting higher and lower ratios.

6.5.2 Zn enrichment

On the whole, Zn exhibited a lower degree of top to sub soil enrichment than the Pb, the sub soil containing on average 30% less total Zn than the top soil. Zn enrichment ratios varied less dramatically than Pb ratios, although a wide range was noted for the reducible Zn fraction (Table 6.8). The residual, least available fraction exhibited the lowest mean ratio, the top soil containing only marginally higher concentrations of this fraction than the sub soil. This result may reflect the inherent immobility of the residual fraction, in addition to the possibility that the majority of Zn at this site is of relatively stable geological origin. The exchangeable and oxidisable fractions displayed similar

average top to sub soil enrichment ratios of approximately 2. All five data sets exhibited positively skewed frequency distributions, although the skew was particularly pronounced for the reducible fraction, whose distribution was affected by two outlying samples (Figures 6.20b and 6.24).

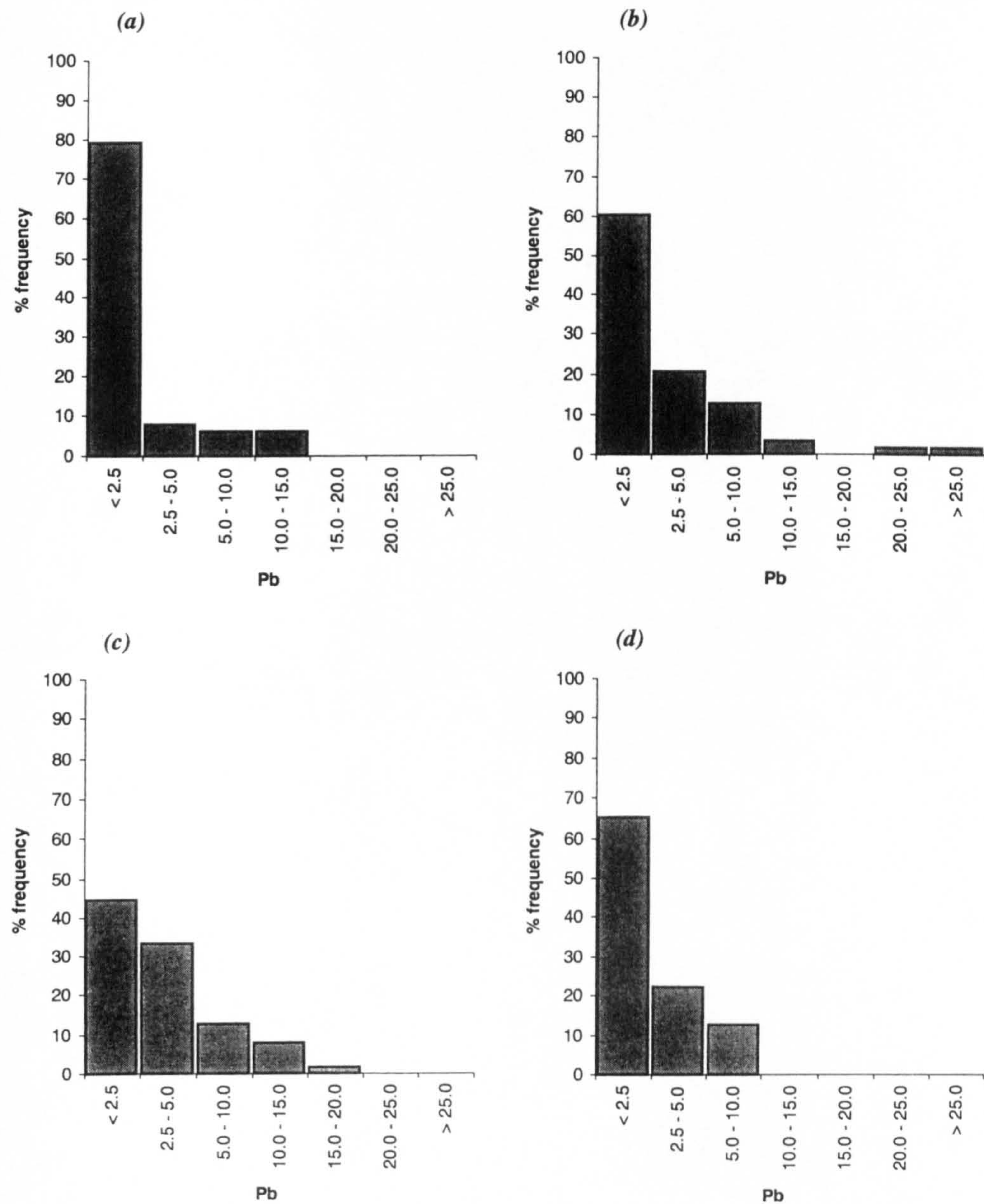


Figure 6.21 Frequency distribution of Pb enrichment ratios (top soil : sub soil), (a) exchangeable; (b) reducible; (c) oxidisable; (d) residual

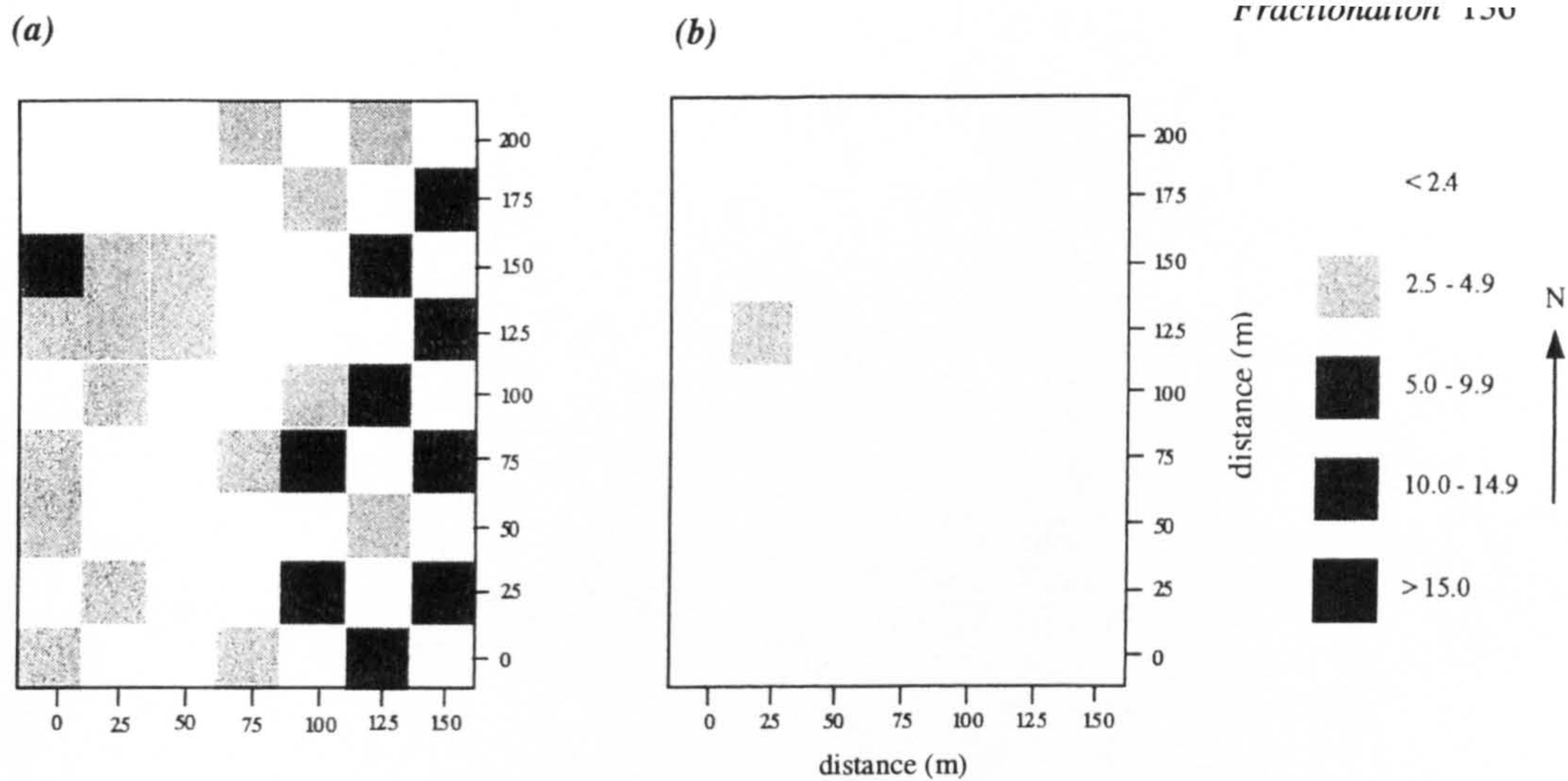
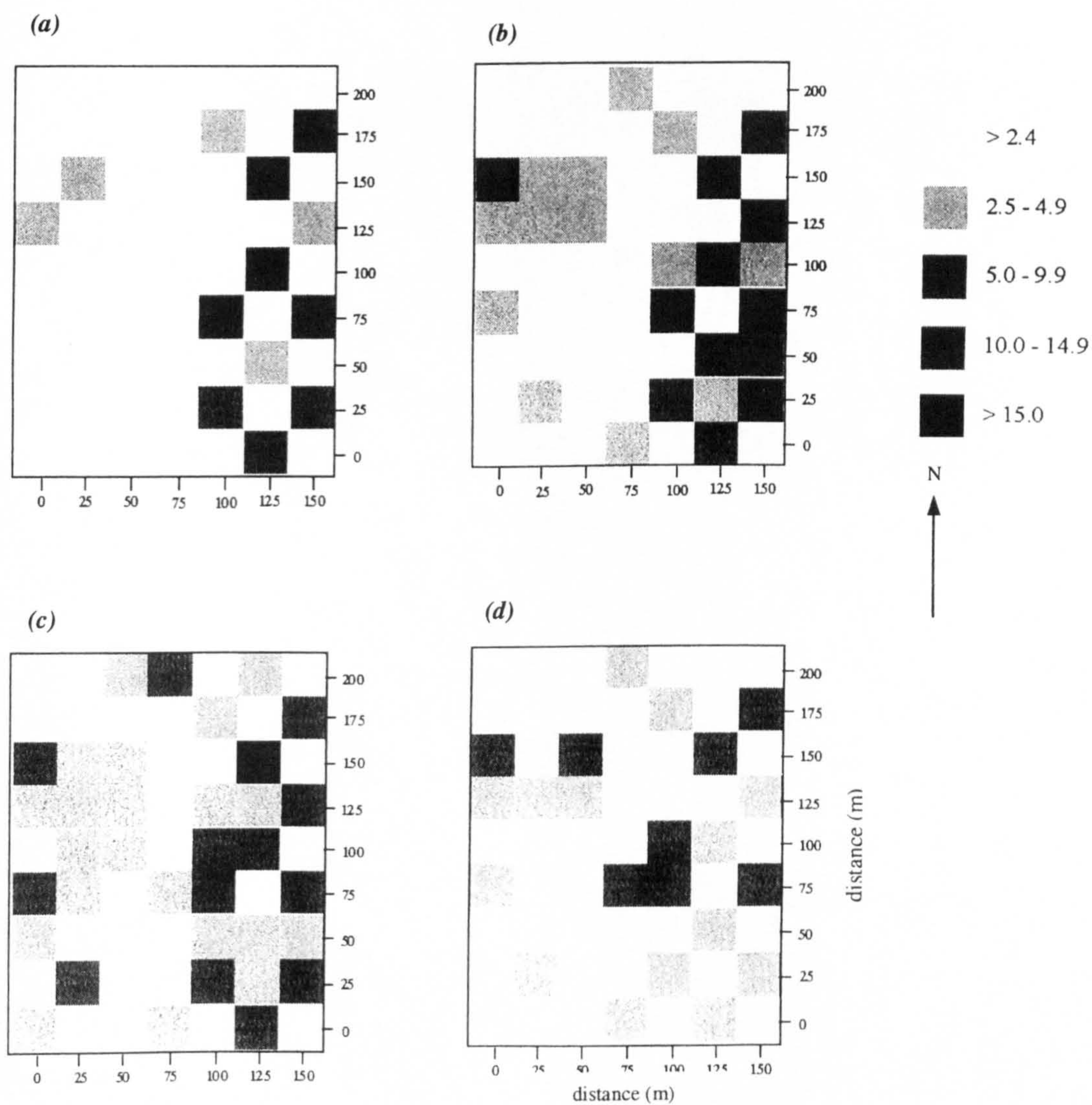


Figure 6.22 Spatial distribution of enrichment ratios (top soil : sub soil), (a) total Pb; (b) total Zn



Zn	total	exchangeable	reducible	oxidisable	residual
mean	1.3	22.2	2.7	1.8	1.2
median	1.2	2.0	1.5	1.5	1.1
s.d.	0.4	1.2	4.2	1.0	0.4
max.	3.2	5.0	28.5	5.2	3.2
min.	0.8	0.4	0.4	0.6	0.8
skewness	3.00	0.62	4.63	1.07	1.44

Table 6.8 Enrichment ratios (top soil : sub soil), Zn

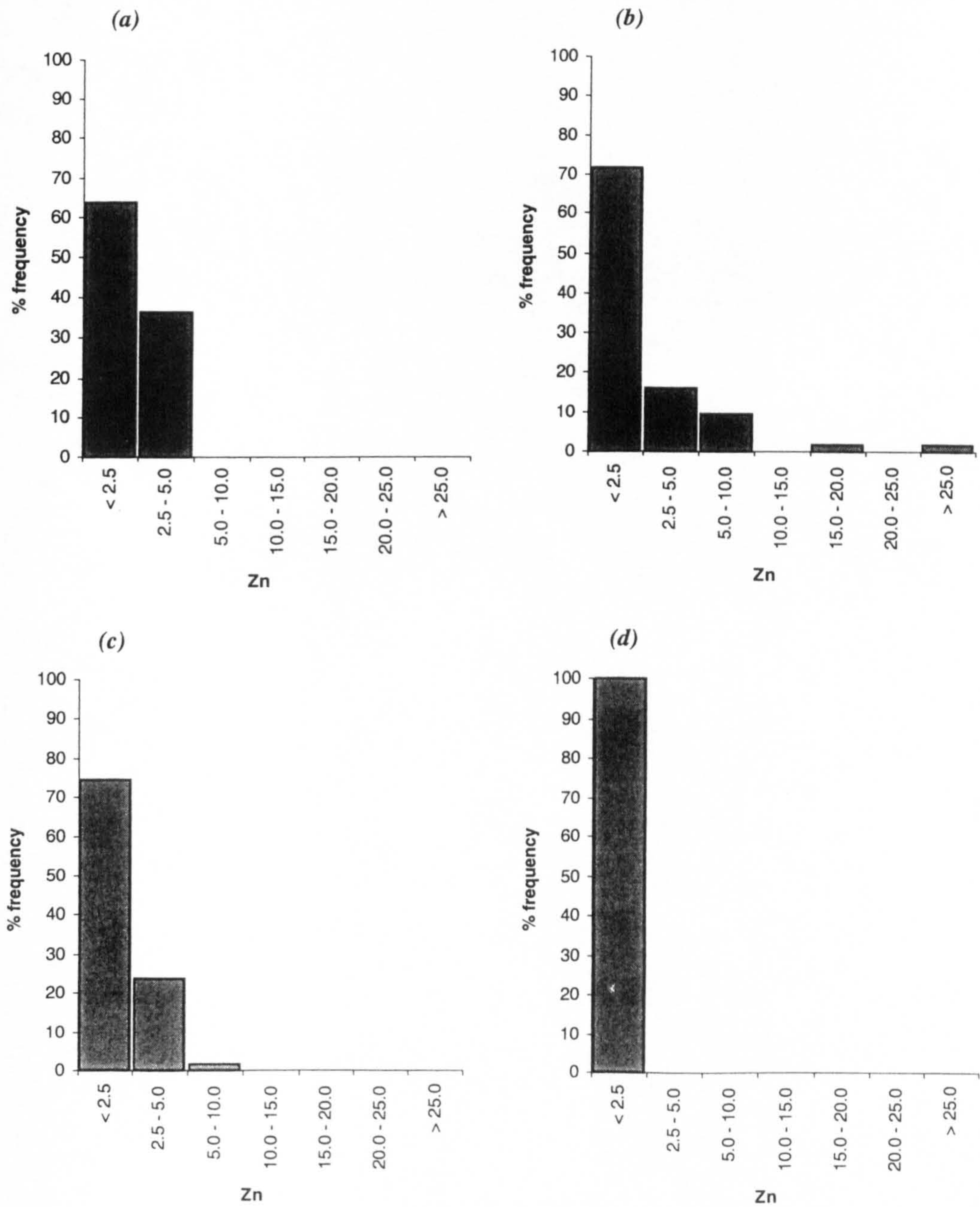


Figure 6.24 Frequency distribution of Zn enrichment ratios (top soil : sub soil), (a) exchangeable; (b) reducible; (c) oxidisable; (d) residual

The spatial distribution of the enrichment ratios exhibited differing patterns for the total Zn and Zn fractions, although in general higher ratios were identified on the western side of the plot. Again, the pattern appeared to be localised or hotspot in nature. The spatial plots identified little or no variation in the total and residual Zn enrichment ratios, only one sample point exhibiting a ratio of > 2.4 , exceeding the cut-off for the first classification on the pixel map (Figures 6.22b and 6.25).

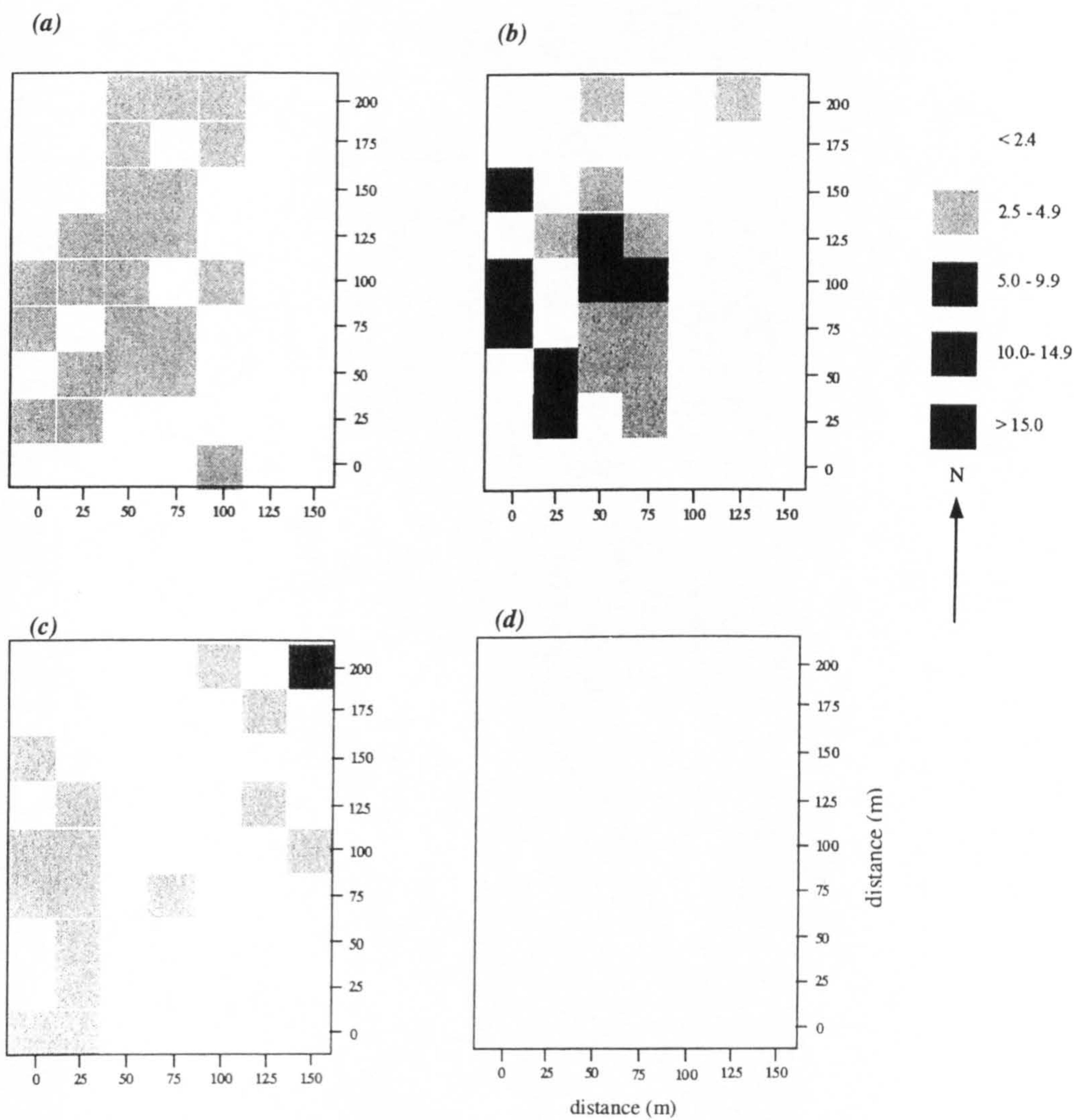


Figure 6.25 Spatial distribution of Zn enrichment ratios (top soil : sub soil), (a) exchangeable; (b) reducible; (c) oxidisable; (d) residual

It was noted that total Pb exhibited a higher top soil to sub soil enrichment ratio than total Zn. The top soil layer contained on average 210% more total Pb and 30% more total Zn than the sub soil. Both metals exhibited similar ratios for the exchangeable fraction, although ratios for reducible, oxidisable and residual Pb were greater than those of the corresponding Zn fractions (Tables 6.6 and 6.7).

6.6 SUMMARY

As for the total metals, a higher degree of variation in concentrations was noted within the Pb than the Zn fractions. In addition, most concentrations were positively skewed with frequency distributions exhibiting many low and few high values. All four Pb fractions displayed similar patterns of spatial distribution that corresponded well with those identified for total Pb. The Zn fractions on the other hand, exhibited different patterns of spatial distribution that did not correspond with those of the total metal. Both metals, total and fractions, exhibited hot spot patterns of spatial distribution.

Top and sub soil Pb displayed a preference for the oxidisable and reducible fractions, the fractions containing on average 37% and 42% of the total Pb. Partitioning was of the order oxidisable > reducible > residual > exchangeable. Despite the exchangeable fraction forming the smallest proportion of the total Pb, it was noted that samples containing high concentrations of total Pb contained relatively high concentrations of the readily available exchangeable fraction. The majority, on average 60%, of total Zn was of the residual form, partitioning being of the order residual > exchangeable > oxidisable > reducible. Differences between Pb and Zn partitioning were not statistically significant.

The majority of the top and sub soil Pb and Zn fractions exhibited variograms that could best be modelled by linear functions, exhibiting no variogram sills. All variograms exhibited relatively large nugget variances indicating that variation was occurring at shorter distances than the smallest lag. The variograms highlighted, by differences in gradient, different levels of spatial dependence between the metal fractions. It was

noted that the more readily available and mobile fractions, in particular exchangeable and reducible Pb, exhibited the strongest spatial dependence, whilst the potentially immobile residual fractions displayed the lowest spatial dependence.

Both metals exhibited top soil to sub soil enrichment, the top soil containing on average 210% more Pb and 30% more Zn than the sub soil. Again a high degree of variation was noted. The spatial distribution was hot spot in nature, exhibiting good correspondence between the Pb but not between the Zn fractions. Enrichment ratios between the top and sub soil Pb fractions were of the order, exchangeable, 2.4, reducible, 3.9, oxidisable, 4.0 and residual, 2.5. The top soil also exhibited Zn enrichment, with the fractions displaying ratios of the order, exchangeable 2.2, reducible 2.7, oxidisable 1.8 and residual 1.2.

CHAPTER 7

BEHAVIOUR OF Pb AND Zn

Summary

This chapter investigates the relationships between the metals, Pb and Zn, and soil properties, pH, organic matter content and cation exchange capacity (CEC) within the top and sub soil layers of plot I. The chapter has been divided into 4 main sections that make inferences about the behaviour of the metals within the soil. Section 7.1, provides an overview of the analyses conducted. Section 7.2 describes the variation in pH, organic matter content and CEC within the soil of plot I, in addition to any relationships between the soil properties. Section 7.3 examines relationships between the metal fractions and soil properties using principal components analysis, non-hierarchical cluster analysis, correlation and regression, whilst Section 7.4 summarises the main findings of the chapter, identifying points for discussion in chapter 8.

7.1 INTRODUCTION

This chapter characterises the top and sub soil layers of plot I in terms of the soil properties, pH, organic matter content and cation exchange capacity (CEC), describing variations in both value and spatial distribution, in addition to examining the inter-relationships between the three properties (Section 7.2). Multivariate, principal components analysis (Section 4.6.2.2, Appendix 8) and non-hierarchical cluster analysis (Section 4.6.2.3, Appendix 9), in association with bivariate, correlation, regression and conditioning (Section 4.6.2.1, Appendix 7), have been used to investigate associations between the metal fractions and the soil properties within and between the top and sub soil layers (Section 7.3). From these relationships, behaviour of the metals within the soil of plot I may be inferred.

7.2 SOIL PROPERTIES

This section describes the variation in three soil properties, pH, organic matter content and CEC, within the top and sub soil layers of plot I, in addition to examining property inter-relationships. Variation has been assessed using means, medians, ranges,

coefficients of skewness and frequency distributions, with patterns of spatial distribution examined using spatial plots (Section 4.5.1). Correlation and regression have been used to investigate associations and determine the form of any relationships between the properties (Section 4.6.2.1).

7.2.1 Variation of soil properties

7.2.1.1 pH

Soil within the top and sub soil layers of plot I was classed as acidic (Baize, 1993), displaying pH values ranging from 3.8 to 6.4 (Table 7.1). The sub soil displayed a marginally lower average pH than the top soil, with both layers exhibiting positively skewed frequency distributions (Figure 7.1). The highest pH values were identified within the north west corner of the plot, although a number of patches exhibiting higher and lower than average pH values were scattered throughout the area (Figure 7.2).

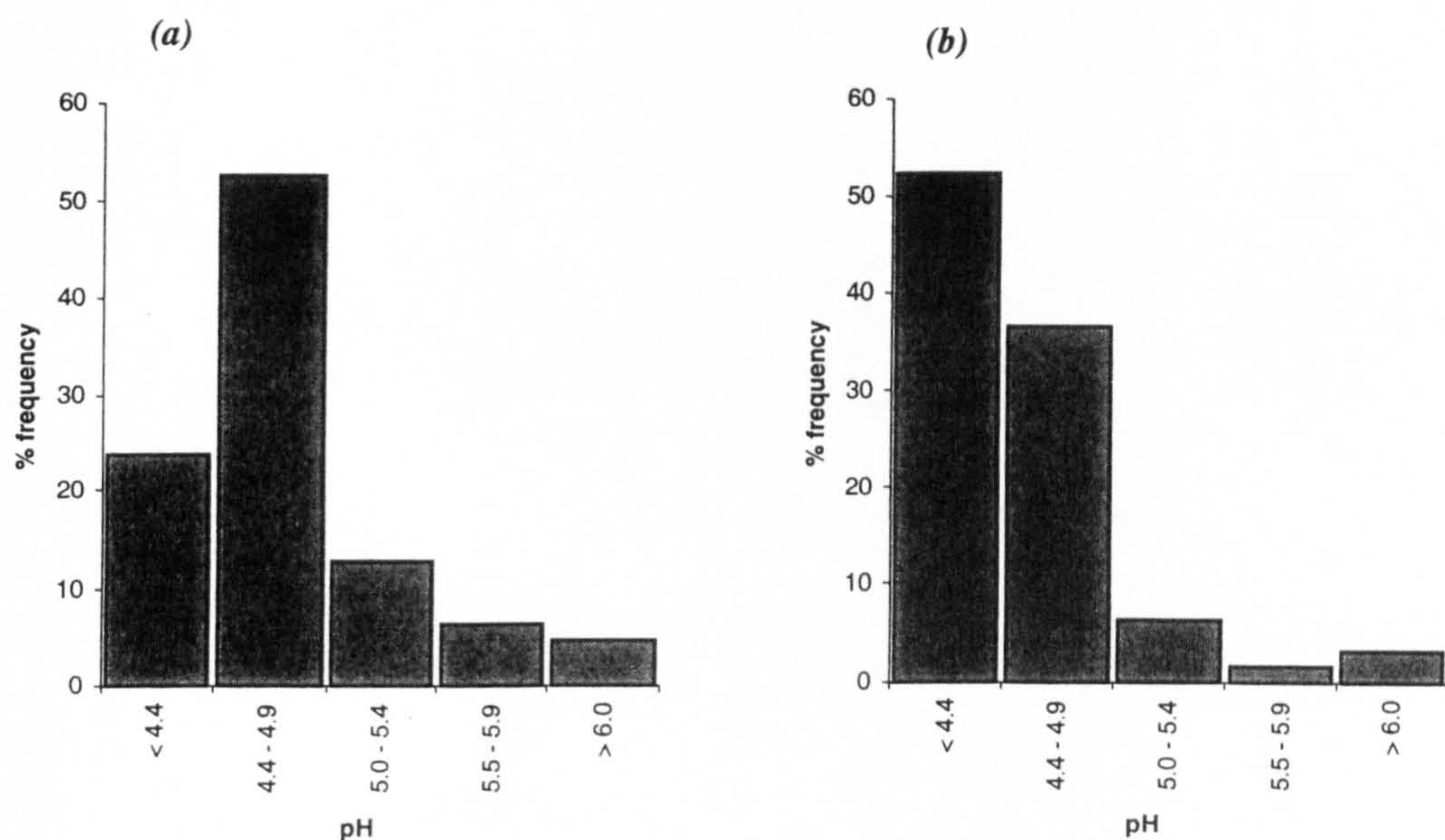


Figure 7.1 Frequency distribution of pH (a) top soil; (b) sub soil

		pH	Organic matter content (%)	CEC (me/100g)
Top soil	mean	4.8	26.3	27.9
	median	4.7	25.1	27.7
	s.d.	0.5	7.5	5.8
	max.	6.3	45.4	40.2
	min.	4.0	13.8	11.8
	skewness	1.12	0.43	-0.07
Sub soil	mean	4.5	13.2	17.4
	median	4.4	13.9	16.9
	s.d.	0.5	2.9	5.2
	max.	6.4	18.1	34.4
	min.	3.8	3.8	9.6
	skewness	1.93	-1.07	1.35

Table 7.1 Summary statistics, soil properties

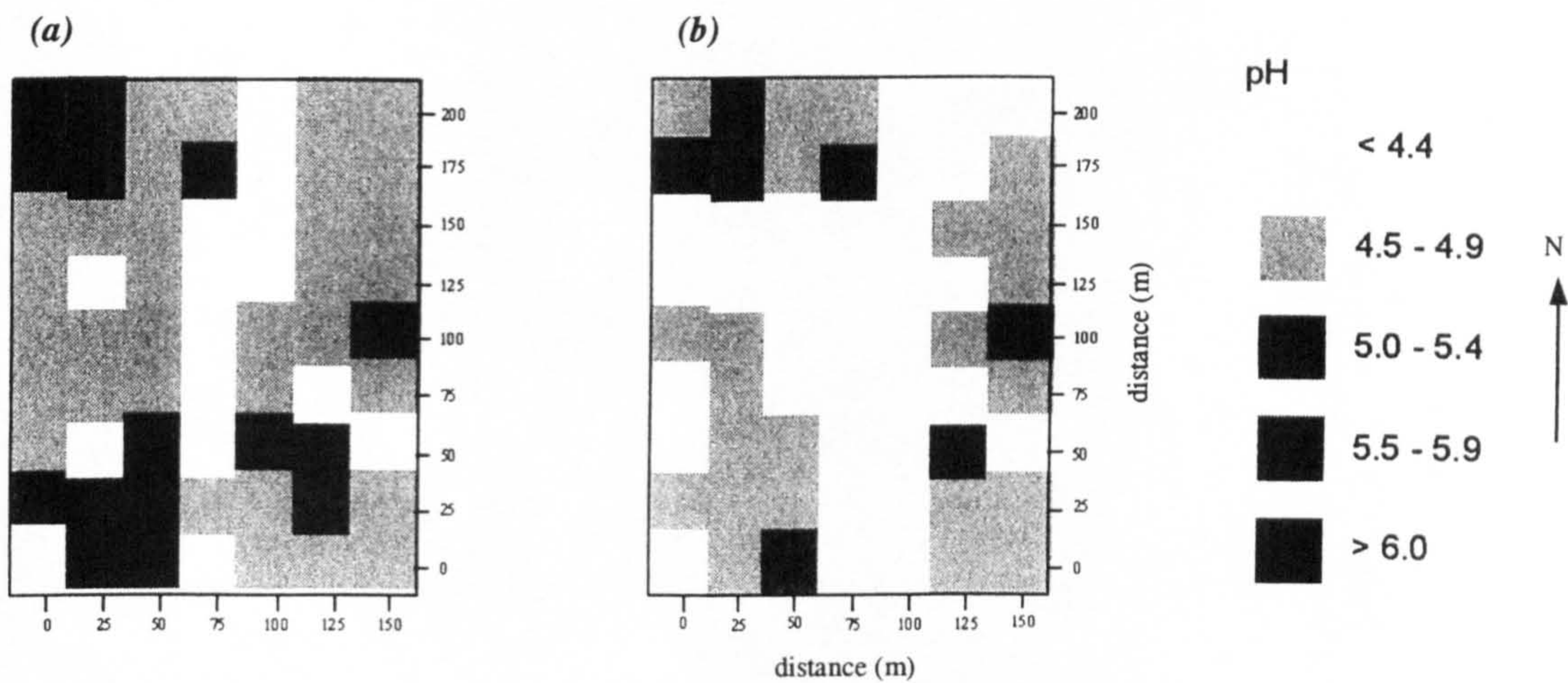


Figure 7.2 Spatial distribution of pH (a) top soil; (b) sub soil

7.2.1.2 Organic matter content

Top soil organic matter content varied dramatically, the top soil layer containing on average twice as much organic matter as the sub soil (Table 7.1). It was noted that organic matter content within the top and sub soil layers exhibited positively and negatively skewed frequency distributions, respectively (Figure 7.3). In contrast to the sub soil, a high degree of spatial variation was seen within the top soil. Higher percentages of top soil organic matter were identified within the south and west of the plot (Figure 7.4).

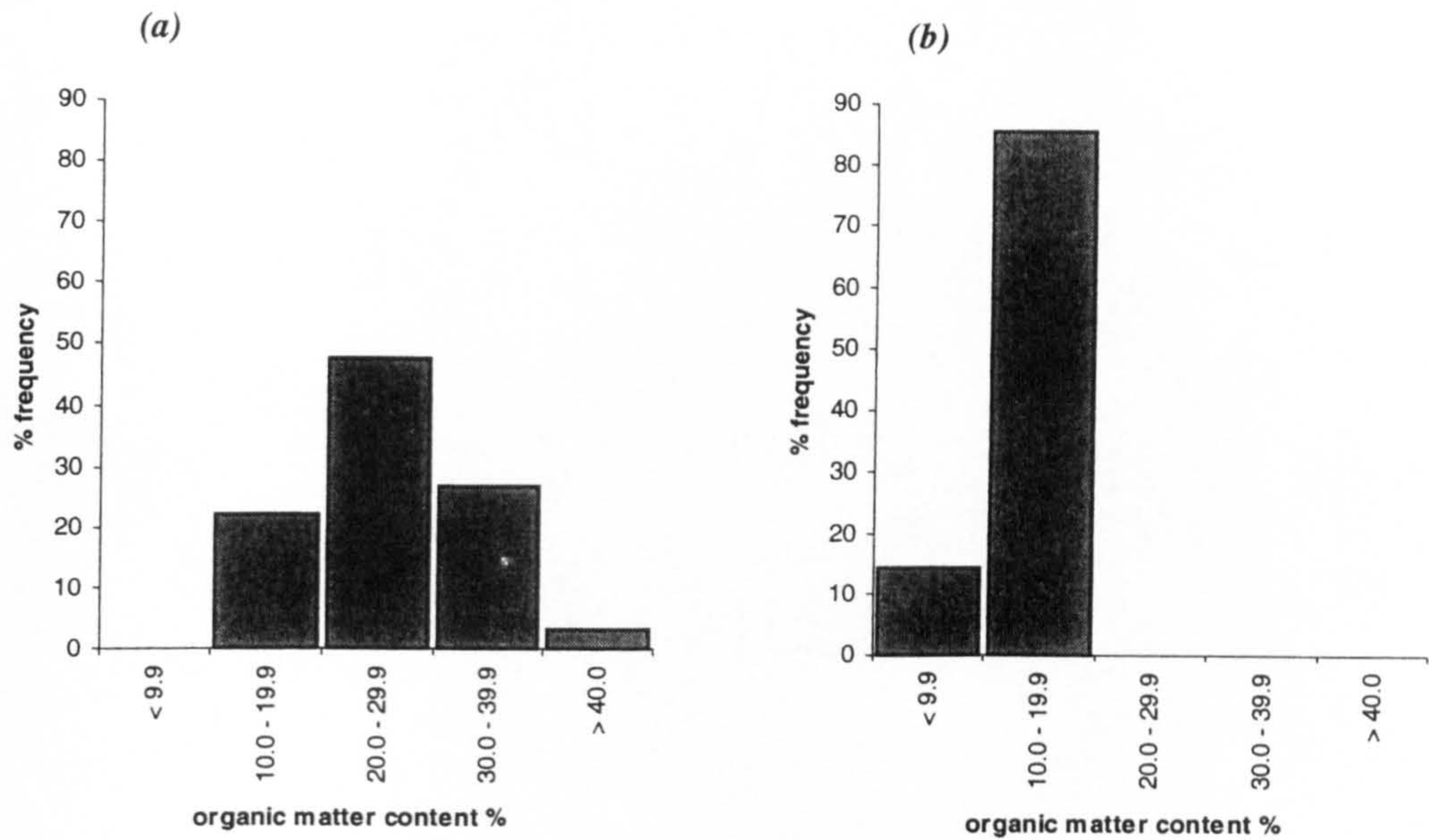


Figure 7.3 Frequency distribution of organic matter content (a) top soil; (b) sub soil

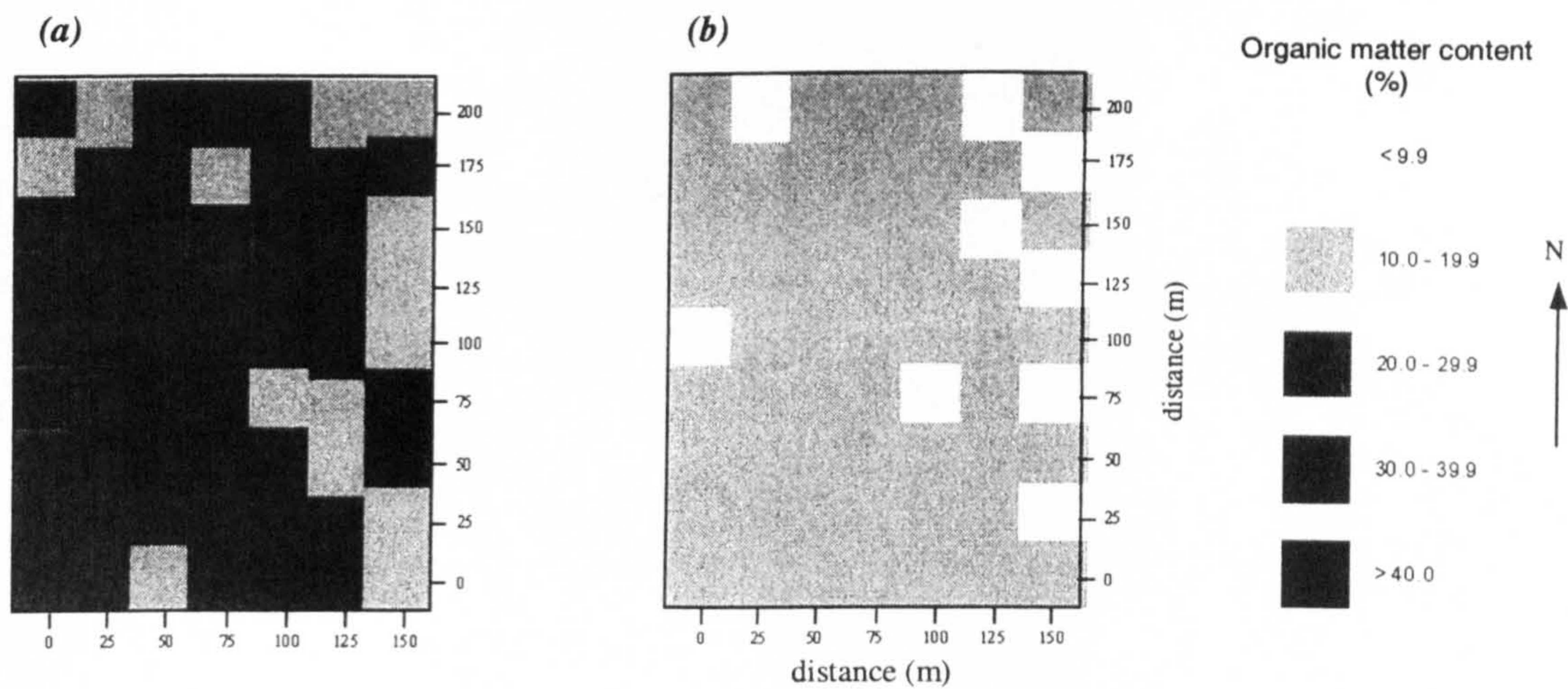


Figure 7.4 Spatial distribution of organic matter (a) top soil; (b) sub soil

7.2.1.3 Cation exchange capacity

The top and sub soil layers were both found to exhibit a wide range of CEC, although on average the top soil exhibited a CEC approximately 10me/100g greater than the sub soil layer (Table 7.1). Both layers displayed positively skewed frequency distributions (Figure 7.5). In general CEC was greatest towards the centre of the plot, however a high degree of spatial variation was noted (Figure 7.6).

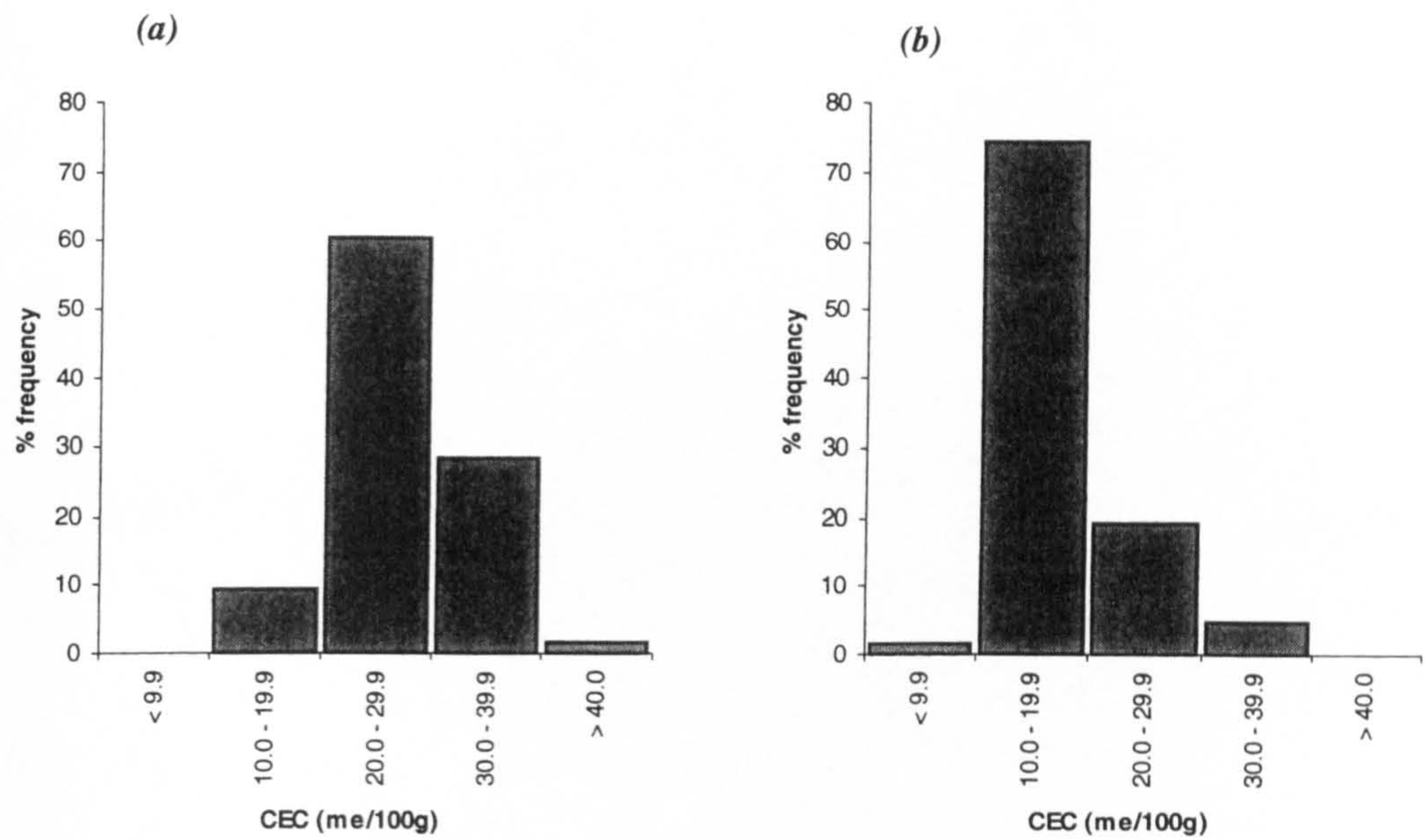


Figure 7.5 Frequency distribution of CEC (a) top soil; (b) sub soil

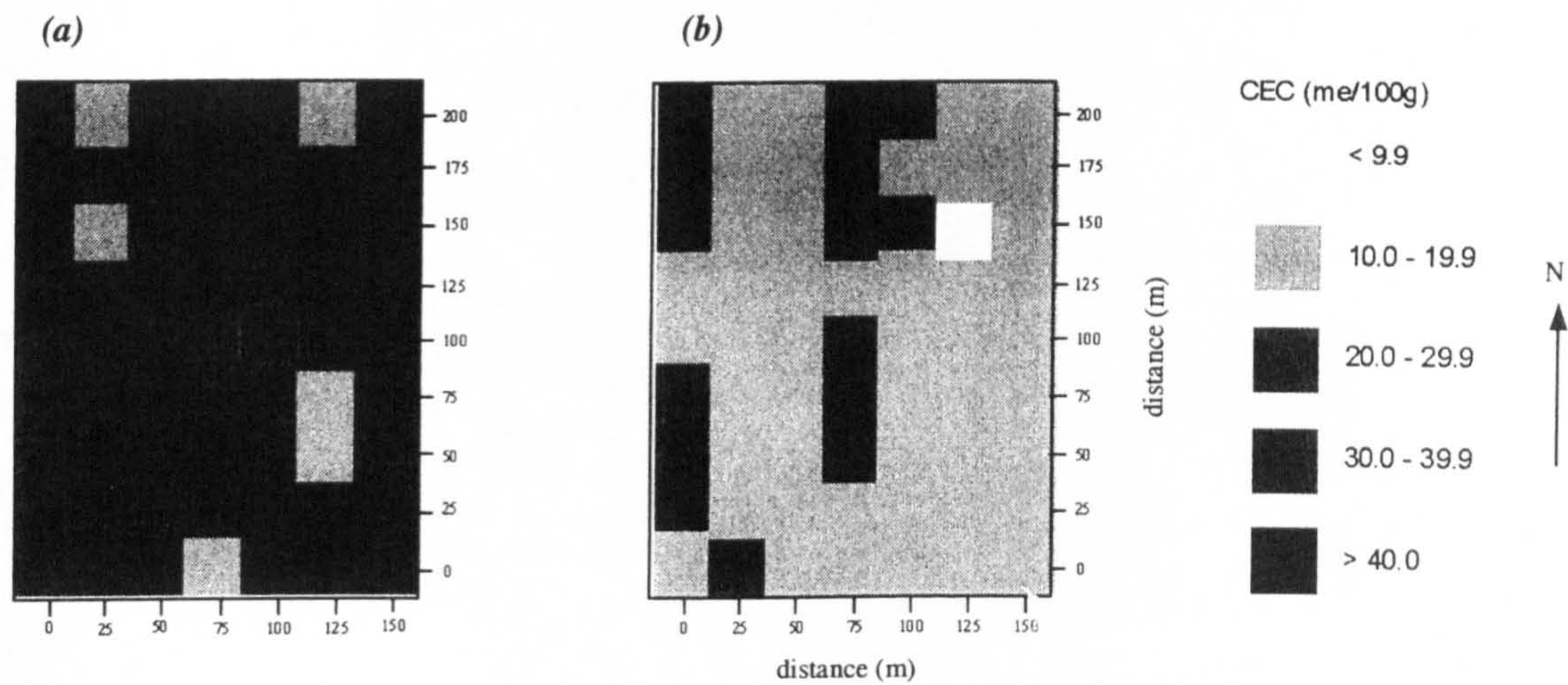


Figure 7.6 Spatial distribution of CEC (a) top soil; (b) sub soil

7.2.2 Relationships between soil properties

The soil properties, pH, organic matter content and CEC displayed several inter-relationships in addition to associations between their top and sub soil values. Those relationships exhibiting correlation coefficients exceeding the 95% ($p<0.05$) critical value, resulting in the rejection of the null hypothesis H_0 (H_0 : no association between variables x and y), are described below. Rejection of H_0 leads to the acceptance of the

alternative hypothesis H_1 , (H_1 : there is an association between x and y), although H_1 is not necessarily true; H_0 only being rejected with a particular degree of certainty.

Due to removal of outlying values, sample size varied between 52 (d.f.=50) and 63 (d.f.=61). The relatively large sample size determined that the critical values for Pearson's Product Moment Correlation coefficients were relatively low (Table 7.2) and hence scatter graphs that appeared to show a high degree of scatter were often found to indicate significant relationships between properties (Table 7.3 defines the abbreviations used). Figure 7.7 shows a matrix scatter plot for all possible soil property inter-relationships and correlation coefficients are displayed in Table 7.4. The strength of associations were described according to the following classification: strong = $|0.75 - 1.0|$; moderate = $|0.45 - 0.75|$; weak = $|< 0.45|$ (Oliver, personal communication). Regression analysis determined that relatively low coefficients of determination (R^2 values) were often found where correlations were weak despite variables exhibiting significant associations.

d.f.	critical values		
	95% ($p < 0.05$)	99% ($p < 0.01$)	99.9% ($p < 0.001$)
50	0.2730	0.3540	0.4430
51	0.2707	0.3511	0.4395
52	0.2654	0.3482	0.4360
53	0.2661	0.3453	0.4325
54	0.2638	0.3424	0.4290
55	0.2615	0.3395	0.4255
56	0.2592	0.3366	0.4220
57	0.2569	0.3337	0.4185
58	0.2546	0.3308	0.4150
59	0.2523	0.3279	0.4115
60	0.2500	0.3250	0.4080
61	0.2484	0.3229	0.4055

Table 7.2 Critical values for Pearsons Product Moment Correlation coefficients

property		abbreviation
top	pH	tph
soil	Organic matter content	tom
	Cation exchange capacity	tcec
sub	pH	sph
soil	Organic matter content	som
	Cation exchange capacity	scec

Table 7.3 Soil property abbreviations

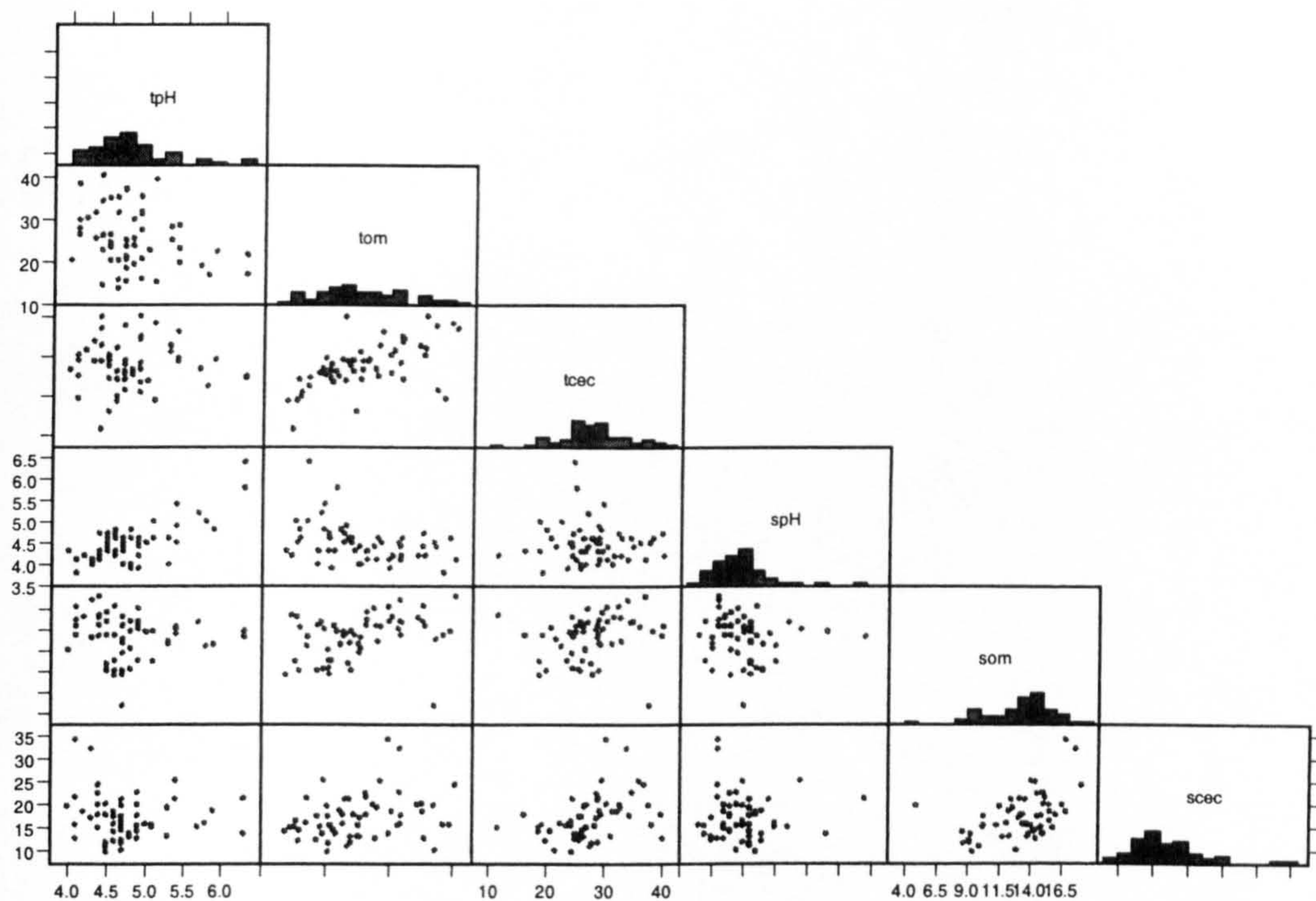


Figure 7.7 Scatter graph matrix depicting frequency distributions and associations between top and sub soil properties

	tpH	tom	tcec	sph	som	sceC
tpH	1.000					
tom	-0.1188 (56)	1.000				
tcec	0.0927 (55)	0.5559*** (62)	1.000			
sph	0.4291** (55)	-0.3451** (59)	-0.0649 (58)	1.000		
som	-0.1363 (55)	0.5142 *** (61)	0.4732*** (60)	-0.2435 (58)	1.000	
sceC	0.0931 (54)	0.3117* (60)	0.4186*** (59)	-0.0058 (56)	0.5414*** (58)	1.000

Table 7.4 Correlation coefficients for soil properties, plot I. 99.9% *** ; 99% ** ; 95% *. n = number in brackets

The soil properties, pH ($p<0.01$), organic matter content ($p<0.001$) and CEC ($p<0.001$) exhibited significant correlations between the top and sub soil layers of plot I, leading to the rejection of the null hypothesis with 99%, 99.9% and 99.9% certainty, respectively. With the exception of organic matter content, which exhibited a moderate correlation, associations were weak (Table 7.4). The correlations were positive and hence sample points displaying higher top soil values had a tendency to display higher sub soil values.

Regression analysis determined that levels of explanation were relatively low, therefore a substantial degree of variation in the sub soil was unaccounted for by variation in the corresponding top soil property alone (Figure 7.8).

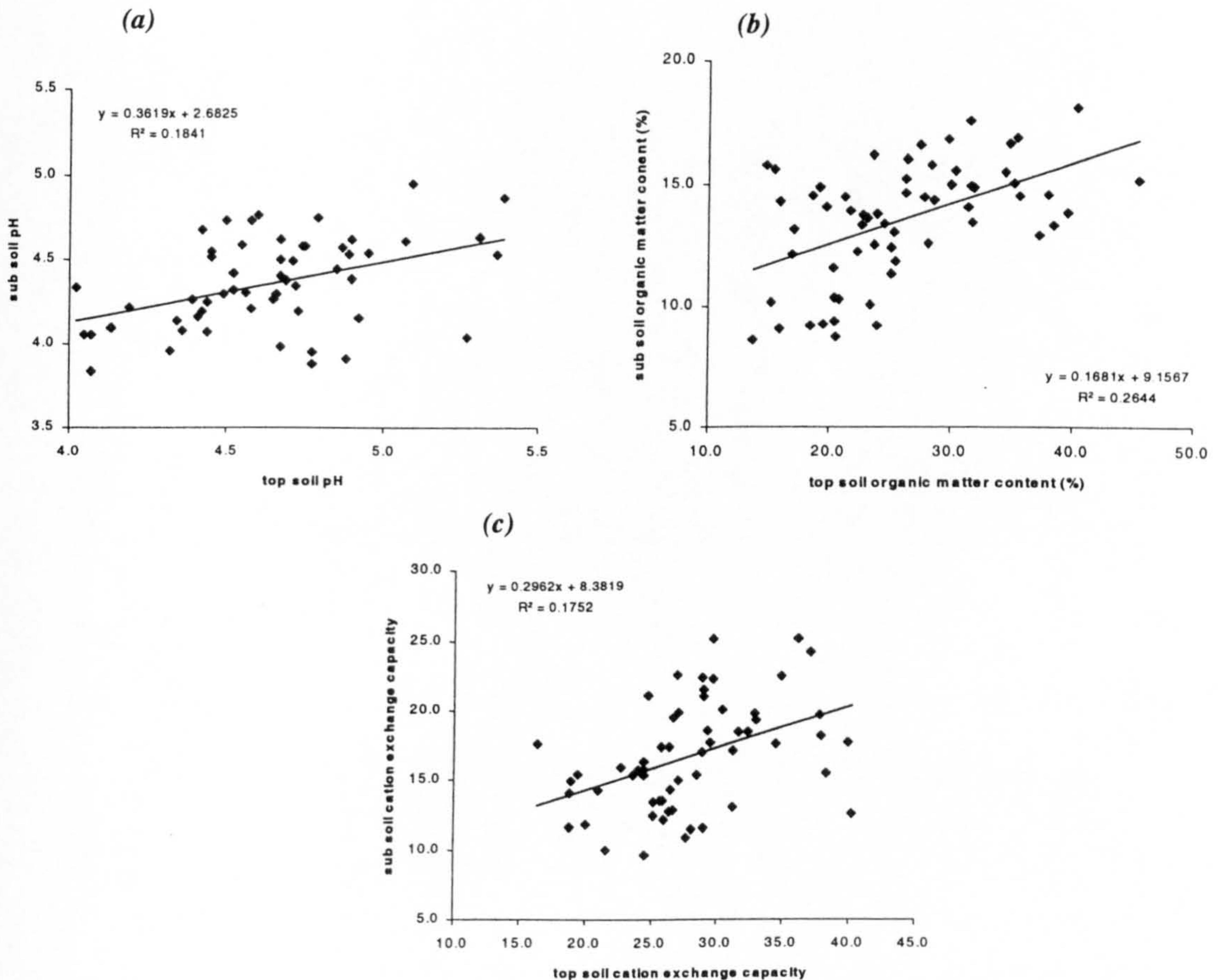


Figure 7.8 relationships between top and sub soil properties, plot I, (a) pH; (b) organic matter content; (c) CEC

Moderate associations, the correlation coefficients of which exceeded the 99.9% ($p < 0.001$) significance level, were also noted between organic matter and CEC within the top and sub soil layers (Table 7.4). Regression analysis determined that R^2 values were similar within both soil layers. Gradients of regression equations indicated that an increase in organic matter content would result in a greater increase in sub soil CEC than top soil CEC (Figure 7.9).

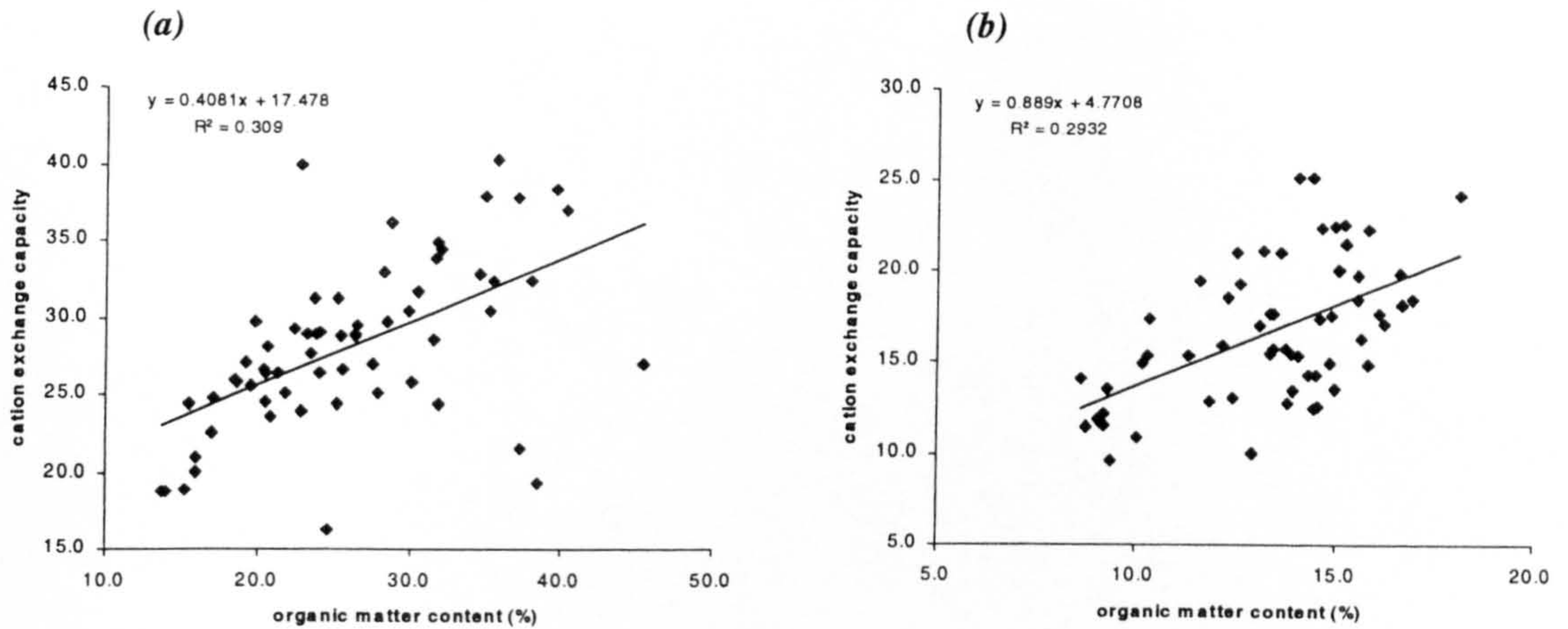


Figure 7.9 Relationship between top and sub soil properties, plot I, (a) top soil organic matter content and CEC; (b) sub soil organic matter content and CEC

7.3 BEHAVIOUR

Behaviour of the heavy metals (Pb and Zn) within the soil of plot I was inferred following the assessment of relationships using PCA (Section 4.6.2.2, Appendix 8), non-hierarchical cluster analysis (Section 4.6.2.3, Appendix 9), correlation and regression (Section 4.6.2.1, Appendix 7). PCA enabled the variables to be reduced to a small number of non-correlated principal components or indices from which factor correlation plots in the planes of PC1 and 2 and PC3 and 4 were considered. These plots enabled the correlation structure of the data to be ascertained, with clusters of points indicating closely related variables. In addition a projection of the site scores in the plane of PC1 and 2 was examined drawing general conclusions as to the similarity / dissimilarity of the samples and identifying outliers. Non-hierarchical analysis was used as a multivariate classification of the sites, as there appeared to be little spatial structure within the plot. When mapped as a pixel map, the classification highlighted relationships between soil variables. Correlation analysis was used to assess the significance and strength of any associations between the variables, using the null hypothesis, H_0 , of no association between variables x and y . Regression analysis determined the level of explanation and form of these relationships. Table 7.5 indicates the abbreviations used.

variable	top soil	sub soil
exchangeable Pb	exc-tpb	exc-spb
reducible Pb	red-tpb	red-spb
oxidisable Pb	oxi-tpb	oxi-spb
residual Pb	res-tpb	res-spb
total Pb	tpb	spb
exchangeable Pb	exc-tzn	exc-szn
reducible Pb	red-tzn	red-szn
oxidisable Pb	oxi-tzn	oxi-szn
residual Pb	res-tzn	res-szn
total Pb	tzn	szn
pH	tpH	spH
organic matter content	tom	som
cation exchange capacity	tcec	scec

Table 7.5 Abbreviations used for Pb and Zn variables and soil properties.

7.3.1 PCA

Correlation based PCA determined that the first 10 factors or principal components (PC) explained 92.24% of the total variance (Table 7.6, Figure 7.10). PC1 to 4 explained a high proportion of the variance with factors 1 and 2 accounting for 30.21 and 15.38%, respectively. Together PC 1 and 2 explained 45.59% of the variance indicating the occurrence of a reasonable degree of correlation between the measured properties. The 3rd and 4th principal components explained the next highest variation, 13.20 and 10.28%. The contribution of the remaining factors was small, approximately 30%, and therefore disregarded from this discussion (Table 7.6, Figure 7.10). Total metals have been excluded from the PCA as it appears logical that correlations will exist between total metals and the metal fractions. Removal of total metals was noted as reducing the % of variance explained by the PCA, however, reduction was marginal.

	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10
eigenvalue	6.646	3.384	2.903	2.262	1.474	1.082	0.809	0.673	0.595	0.467
% variance explained	30.21	15.38	13.20	10.28	6.70	4.92	3.68	3.06	2.71	2.11
cumulative explained variance	30.21	45.59	58.79	69.07	75.77	80.69	84.37	87.43	90.13	92.24

Table 7.6 Eigenvalues and % explained variance of first 10 principal components

Barona and Romero (1996) define factor loading as the extent to which each variable correlates with each of the factors or principal components, stating that there are no widely accepted statistical standards regarding what constitutes a high or low loading. In their research the authors classed variables exhibiting a coefficient of between |1.0 -

0.7| as being significantly correlated with a factor or principal component, as specified by Heberger *et al.* (1994). This classification was also used in this study.

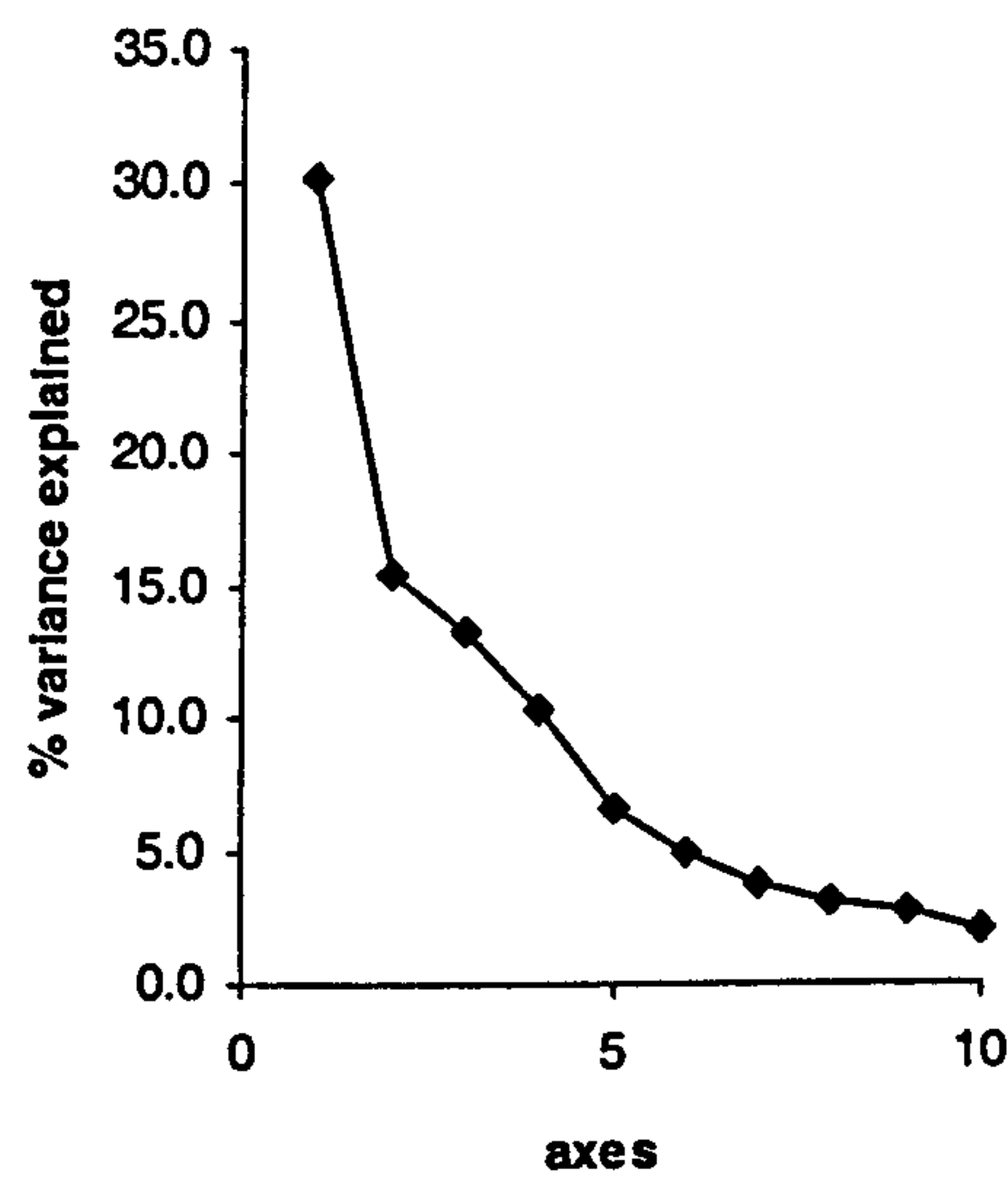


Figure 7.10 Explained variance of principal axes (components)

Correlations between the variables and the principal components PC1 and 2 and PC3 and 4 are displayed in Figure 7.11, the area outside the shaded square representing the statistically significant zone. Correlation coefficients are also shown in Table 7.7 with those variables significantly correlated with PC1 to 4 highlighted in boldface. PC1 exhibited strong correlations with many of the Pb fractions (red-tpb, oxi-tpb, res-tpb, exc-spb, red-spb, oxi-spb), although no associations were seen with Zn fractions or soil properties. PC1 was dominated by these variables, the single cluster indicating that correlation coefficients between the variables will be relatively high. The variables exhibiting statistically significant associations appeared on the negative side of the factor 1 axes, with no variables counteracting the metal distribution pattern by appearing on the positive side of the axis (Figure 7.11). Factor 2 (PC2) on the other hand, correlated with only 1 variable, top soil reducible Zn (red-tzn). No variables exhibited strong correlations with factors 3 and 4 (Figure 7.11, Table 7.7); hence only the first 2 principal components have been considered from here onwards.

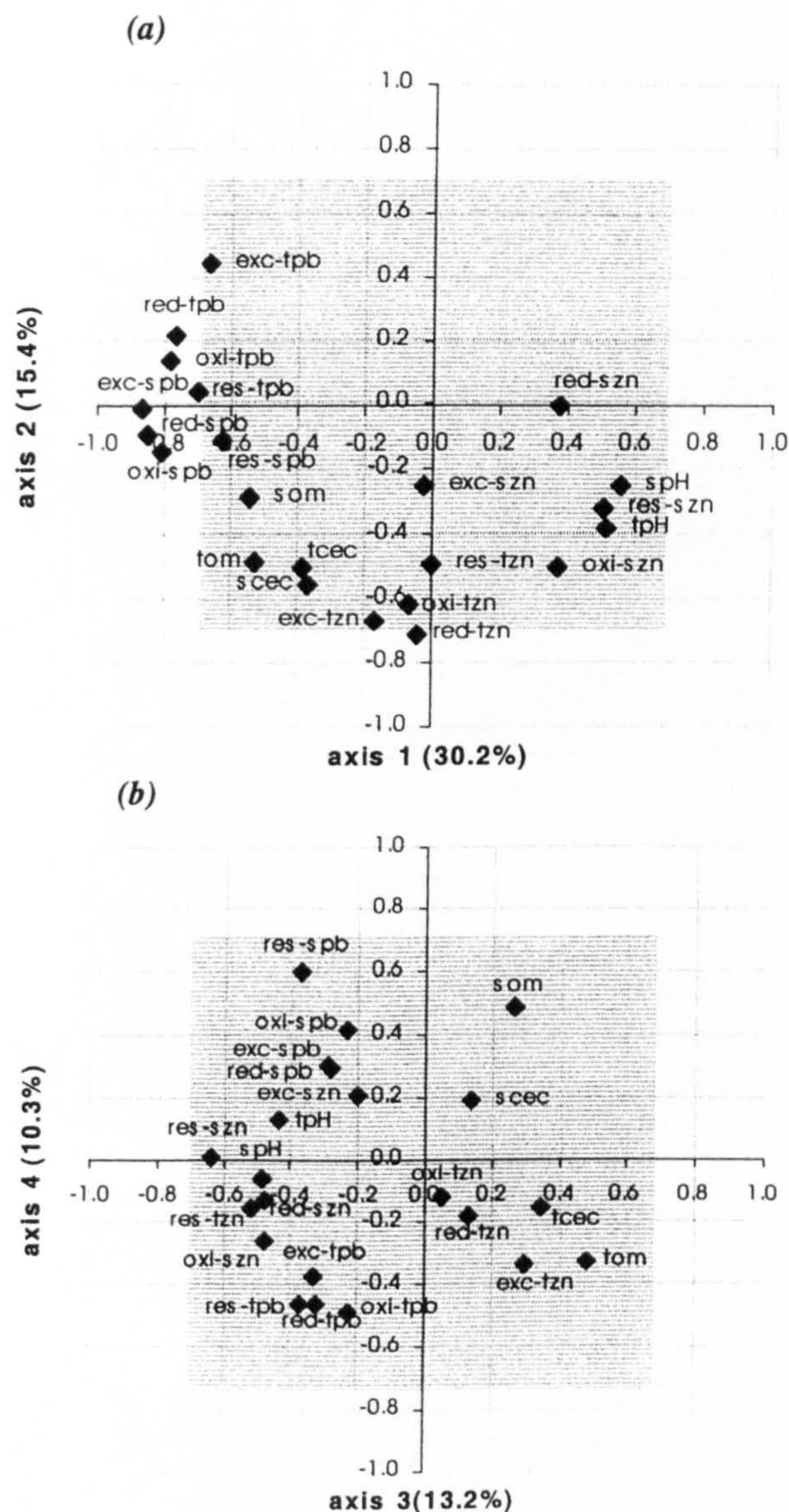


Figure 7.11 Projection of variables in (a) PC1 and PC2; (b) PC3 and PC4

The plot of site scores in the plane of PC1 and PC2 displays no obvious clustering (Figure 7.12). The sampling sites are fairly evenly distributed in the projection, although a number of outliers, exhibiting potentially different characteristics have been highlighted; these include S1, S18, S31 and S51. Samples S31 and S51 are located towards the negative end of PC1 exhibiting high concentrations of top and sub soil Pb fractions. S18 on the other hand is located towards the positive end of the axis indicating low concentrations of Pb. Sample S1 is located at the negative end of PC2 and hence characterised by a higher concentration of top soil reducible Zn. The pixel

maps, exhibiting spatial distribution of the variables (Chapters 5, 6 and 7) also highlight these patterns.

Correlation coefficients with principal components

variable	PC1	PC2	PC3	PC4
exc-tpb	-0.663	0.443	-0.330	-0.372
red-tpb	-0.763	0.212	-0.319	-0.465
oxi-tpb	-0.781	0.135	-0.223	-0.485
res-tpb	-0.704	0.036	-0.368	-0.459
exc-spb	-0.866	-0.010	-0.286	0.297
red-spb	-0.854	-0.093	-0.287	0.306
oxi-spb	-0.808	-0.147	-0.237	0.417
res-spb	-0.628	-0.112	-0.370	0.599
exc-tzn	-0.168	-0.666	0.297	-0.339
red-tzn	-0.042	-0.712	0.129	-0.179
oxi-tzn	-0.070	-0.618	0.047	-0.120
res-tzn	0.001	-0.496	-0.515	-0.16
exc-szn	-0.024	-0.249	-0.201	0.209
red-szn	0.371	-0.005	-0.477	-0.131
oxi-szn	0.371	-0.500	-0.478	-0.264
res-szn	0.512	-0.315	-0.641	0.012
tpH	0.516	-0.383	-0.437	0.131
tom	-0.523	-0.483	0.486	-0.333
tcec	-0.380	-0.504	0.349	-0.155
spH	0.556	-0.249	-0.481	-0.065
som	-0.542	-0.288	0.265	0.488
scec	-0.367	-0.558	0.141	0.194

Figure 7.7 Correlation coefficients with principal components. Values in bold type are strong correlations (>|0.7|).

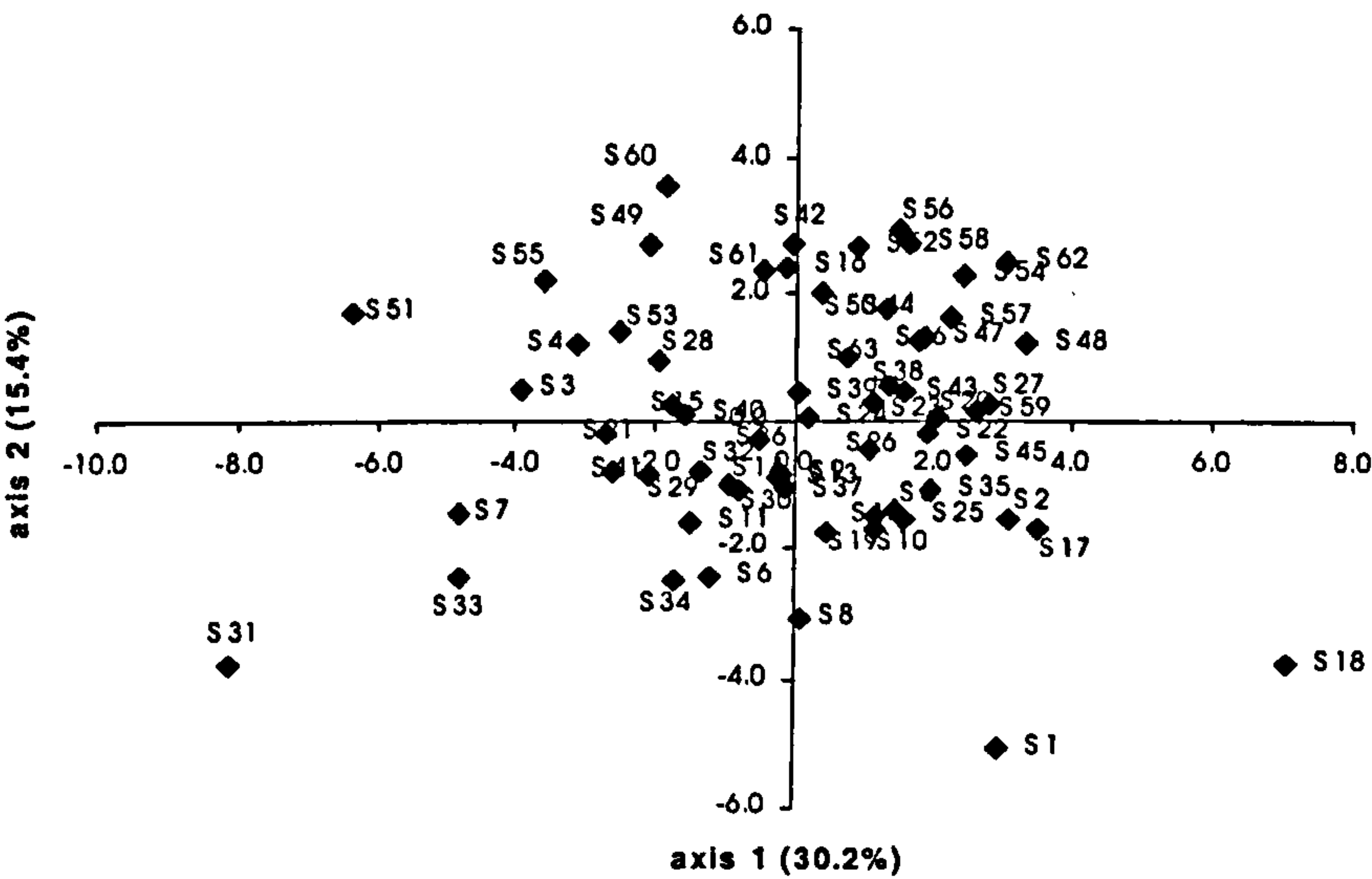


Figure 7.12 Projection of site scores in the plane of PC1 and PC2

7.3.2 Non-hierarchical cluster analysis

The projection of PCA eigenscores in the plane of PC1 and PC2, in addition to the lack of spatial structure identified by the production of variograms, indicates a lack of clustering within the plot I data. Non-hierarchical analysis was therefore used, as a multivariate clustering technique, to further examine the data in an attempt to identify groups of samples exhibiting similar characteristics (Section 4.6.2.3, Appendix 9). Pixel maps classifying sites according to their non-hierarchical class were used to investigate spatial patterns. Due to the non-clustered nature of the data any optimised classifications are likely to be local rather than global.

Initially all 26 variables and 63 sites were included within the cluster analysis, however due to the non-clustered nature of this data (Figure 7.12) a single optimum classification could not be reached despite a large number of classes being examined. This result indicates a lack of association between Pb and Zn fractionation and soil properties within plot I. The analysis was therefore conducted using a smaller number of variables for each of the 63 sites. Individual classifications were determined for Pb and Zn fractions within the top and sub soil layers. Table 7.8 summaries the optimum number of classes for each analysis, determined via the examination of graphs of L^2g versus g , where L represents the Wilks criterion and g the number of clusters (Appendix 9). The optimum number of classes varied for each set of variables, ranging between 4 and 6.

variables	optimum number of clusters
top soil Pb fractions	4
sub soil Pb fractions	4
top and sub soil Pb fractions	4
top soil Zn fractions	5
sub soil Zn fractions	3
top and sub soil Zn fractions	6

Table 7.8 Optimum number of classes for various non-hierarchical classifications

The mean class characteristics for each analysis are summarised in Tables 7.9 and 7.10. In general, the clusters representing Pb partitioning within the top and sub layers of the soil were characterised by consistently higher, lower or moderate mean concentrations of all four Pb fractions (Table 7.9). These clusters highlighted the fact that samples

tended to contain consistently higher or lower concentrations of all four Pb fractions (Figures 6.3 and 6.6). Optimum clusters defined for Zn fractionation, on the other hand, displayed variable characteristics (Table 7.10). A cluster exhibiting a high concentration of one fraction, for example, did not necessarily exhibiting a high concentration of the remaining three fractions. There appears to be no pattern to the cluster characteristics highlighting the non-correspondence of high and low concentrations as exhibited by the spatial plots for Zn fractionation (Figures 6.10 and 6.13).

top soil Pb fractions	1	2	3	4
exc-tPb	286.6	30.5	123.4	258.7
red-tPb	1607.5	202.8	652.7	1032.4
oxi-tPb	1770.5	247.8	814.6	1048.5
res-tPb	415.2	62.6	130.0	186.5
sub soil Pb fractions	1	2	3	4
exc-sPb	17.6	242.4	33.7	86.3
red-sPb	68.9	667.9	128.7	258.0
oxi-sPb	73.7	507.5	144.4	245.3
res-sPb	31.1	114.7	48.7	63.3
top and sub soil Pb fractions	1	2	3	4
exc-tPb	231.6	43.9	52.8	237.5
red-tPb	1130.6	256.1	351.5	1091.2
oxi-tPb	1242.8	339.2	458.9	1181.9
res-tPb	230.8	69.9	88.3	259.6
exc-sPb	80.8	22.8	83.8	244.7
red-sPb	229.2	97.5	238.3	702.7
oxi-sPb	184.0	111.5	257.5	529.2
res-sPb	46.8	41.4	70.9	116.8

Table 7.9 Mean concentrations of Pb fractions (mg/kg) for each class identified using a non-hierarchical procedure

On the whole the Pb clusters lacked spatial coherence when mapped, neighbouring samples often belonging to different classes. However, the pixel maps depicting the non-hierarchical classes for the top and sub soil fractions exhibited similar spatial patterns to those displaying total and fractional Pb concentrations (Figures 5.8, 6.3, 6.6 and 7.13). Some similarities were also seen between the spatial distribution of Zn non-hierarchical classes and Zn concentrations (Figures 5.10, 6.10, 6.13 and 7.14), although these were less marked. As the algorithm takes no account of the spatial location of the samples this result again suggests strong relationships between fractional Pb concentrations within the plot. Zn concentrations were less strongly associated. The

failure of the technique to identify distinct clusters of samples based on the full data set indicated a lack of correspondence between certain of the variables, e.g. Pb and Zn concentrations.

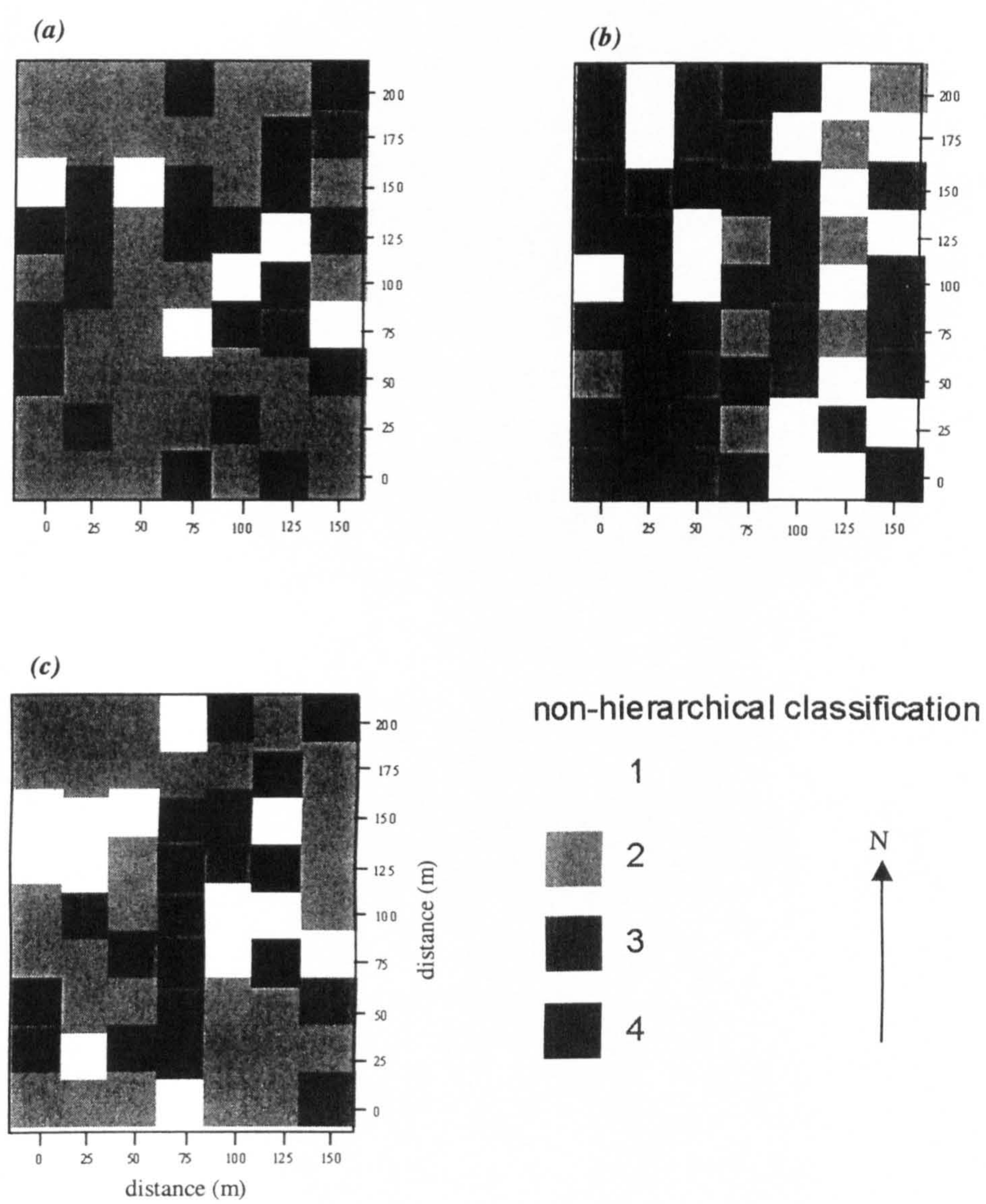


Figure 7.13 Pixel maps depicting the non-hierarchical classes for plot I variables, (a) top soil Pb fractions; (b) sub soil Pb fractions; (c) top and sub soil Pb fractions

top soil Zn fractions	1	2	3	4	5	
exc-tZn	15.2	19.6	14.3	11.9	5.7	
red-tZn	4.8	10.5	8.5	5.1	3.0	
oxi-tZn	18.7	10.6	20.0	6.5	8.9	
res-tZn	42.5	42.1	84.2	44.0	30.8	
sub soil Zn fractions	1	2	3			
exc-sZn	11.3	6.3	5.0			
red-sZn	9.5	2.3	6.3			
oxi-sZn	21.3	6.5	6.5			
res-sZn	71.1	34.4	38.4			
top and sub soil Zn fractions	1	2	3	4	5	6
exc-tZn	15.2	16.5	15.1	19.0	5.3	9.0
red-tZn	4.5	10.9	7.6	10.0	2.4	4.1
oxi-tZn	11.6	22.1	15.6	10.4	9.8	7.6
res-tZn	41.5	25.9	94.4	41.3	33.9	41.1
exc-sZn	9.1	11.3	4.9	4.8	5.2	5.3
red-sZn	4.9	1.8	6.4	401	9.6	2.7
oxi-sZn	7.0	21.3	8.2	6.7	4.0	6.5
res-sZn	30.9	71.1	43.4	35.2	36.8	37.6

Table 7.10 Mean concentrations of Zn fractions (mg/kg) for each class identified using a non-hierarchical procedure

7.3.3 Relationships

7.3.3.1 Pb

Top soil

Within the top soil layer, PCA indicated that as expected the four Pb fractions (exchangeable, reducible, oxidisable and residual) exhibited inter-relationships, the variables forming a cluster towards the left hand side of the projection. Exchangeable Pb was however slightly removed from the main group. When measuring from the origin, small angles were noted between the four fractions suggesting a high degree of correlation (Figure 7.15) (Eigenvalues for the PCA are shown in Table 7.11). Correlation analysis confirmed the strong associations between the Pb variables, determining that the null hypothesis, H_0 , of no association, could be rejected with 99.9% ($p<0.001$) certainty. All correlation coefficients exceeded 0.8000, the strongest association being identified between total and reducible Pb (Table 7.12). Scatter graphs depicting these associations displayed a low degree of scatter (Figure 7.16). All relationships displayed positive coefficients hence variable y increased as variable x increased.

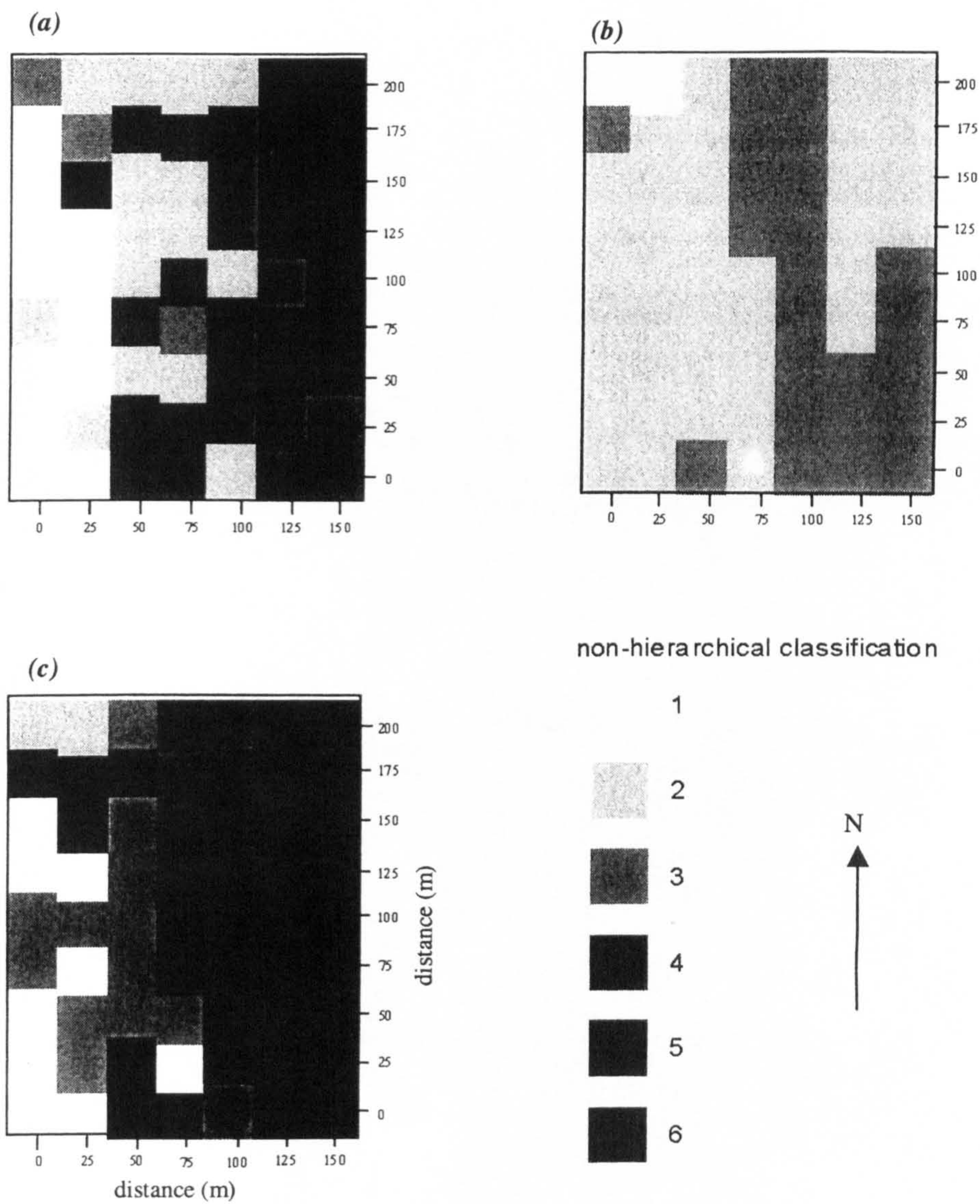


Figure 7.14 Pixel maps depicting the non-hierarchical classes for plot I variables, (a) top soil Pb fractions; (b) sub soil Pb fractions; (c) top and sub soil Pb fractions

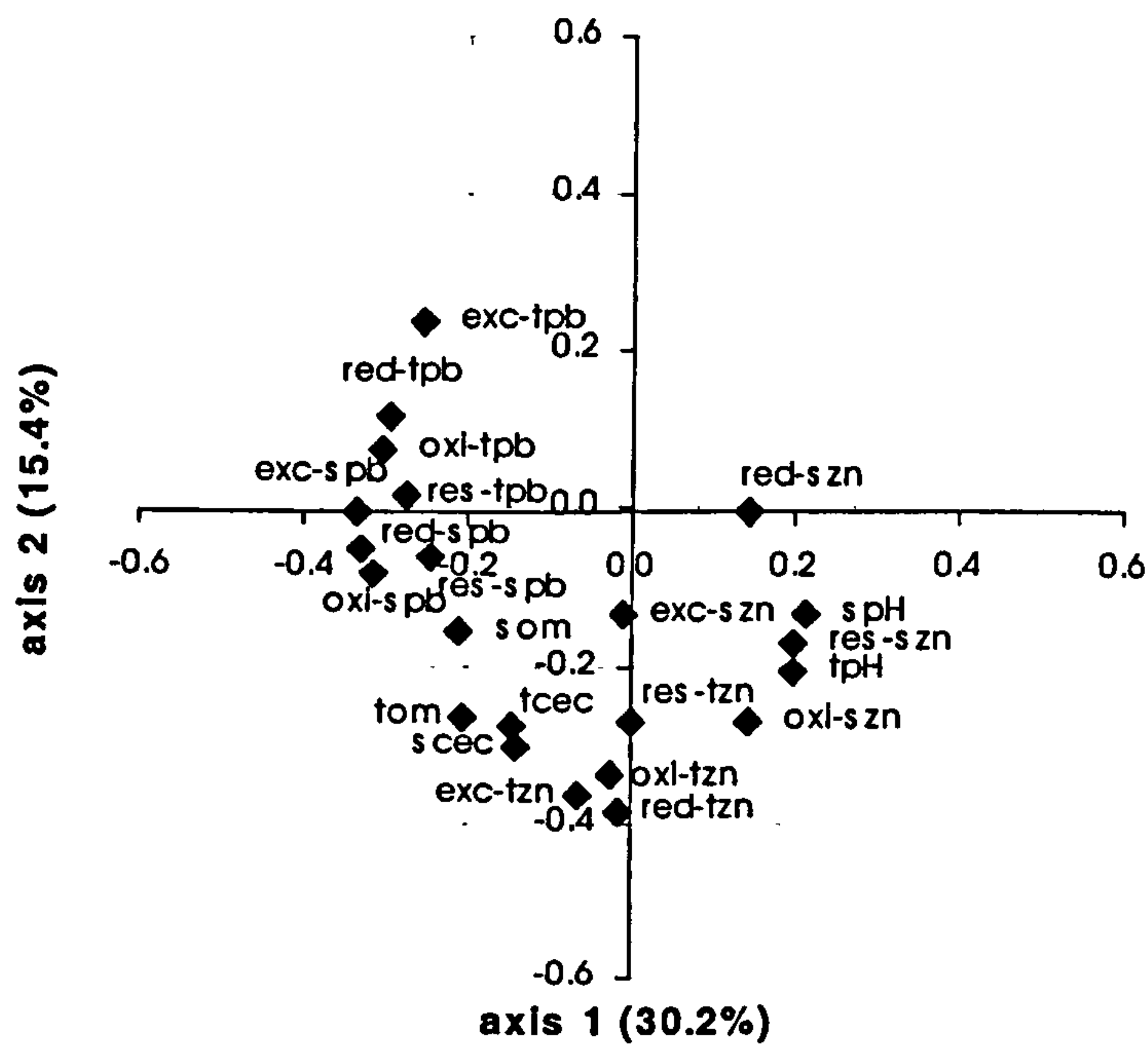


Figure 7.15 Projection of variables in the plane of PC1 and PC2

variable	eigenvalues	
	axis 1	axis 2
exc-tpb	-0.2574	0.2407
red-tpb	-0.296	0.1155
oxi-tpb	-0.3028	0.0736
res-tpb	-0.2732	0.0195
exc-spb	-0.3358	-0.0052
red-spb	-0.3312	-0.0507
oxi-spb	-0.3134	-0.0797
res-spb	-0.2435	-0.061
exc-tzn	-0.065	-0.3621
red-tzn	-0.0162	-0.387
oxi-tzn	-0.0272	-0.3361
res-tzn	0.0004	-0.2697
exc-szn	-0.0094	-0.1351
red-szn	0.144	-0.0025
oxi-szn	0.1438	-0.272
res-szn	0.1986	-0.1713
tph	0.2001	-0.2085
tom	-0.2027	-0.2625
tcec	-0.1474	-0.274
sph	0.2157	-0.1351
som	-0.2101	-0.1566
scec	-0.1422	-0.3031

Table 7.11 Eigenvalues for axes 1 and 2

	exc-tpb	red-tpb	oxi-tpb	res-tpb	tpb
exc-tpb	1.000				
red-tpb	0.9010*** (60)	1.000			
oxi-tpb	0.8138*** (62)	0.9384*** (61)	1.000		
res-tpb	0.8061*** (58)	0.8713*** (58)	0.8735*** (58)	1.000	
tpb	0.8801*** (59)	0.9772*** (59)	0.9713*** (59)	0.8997*** (57)	1.000
tph	-0.2498 (55)	-0.1766 (54)	-0.1313 (56)	-0.2799* (62)	-0.1755 (52)
tom	0.1098 (62)	0.1916 (61)	0.4091*** (63)	0.1298 (57)	0.2855* (59)
tcec	0.0316 (61)	0.0884 (60)	0.2902* (62)	0.0149 (57)	0.1493 (58)

Table 7.12 Correlation coefficients for top soil Pb, plot I.

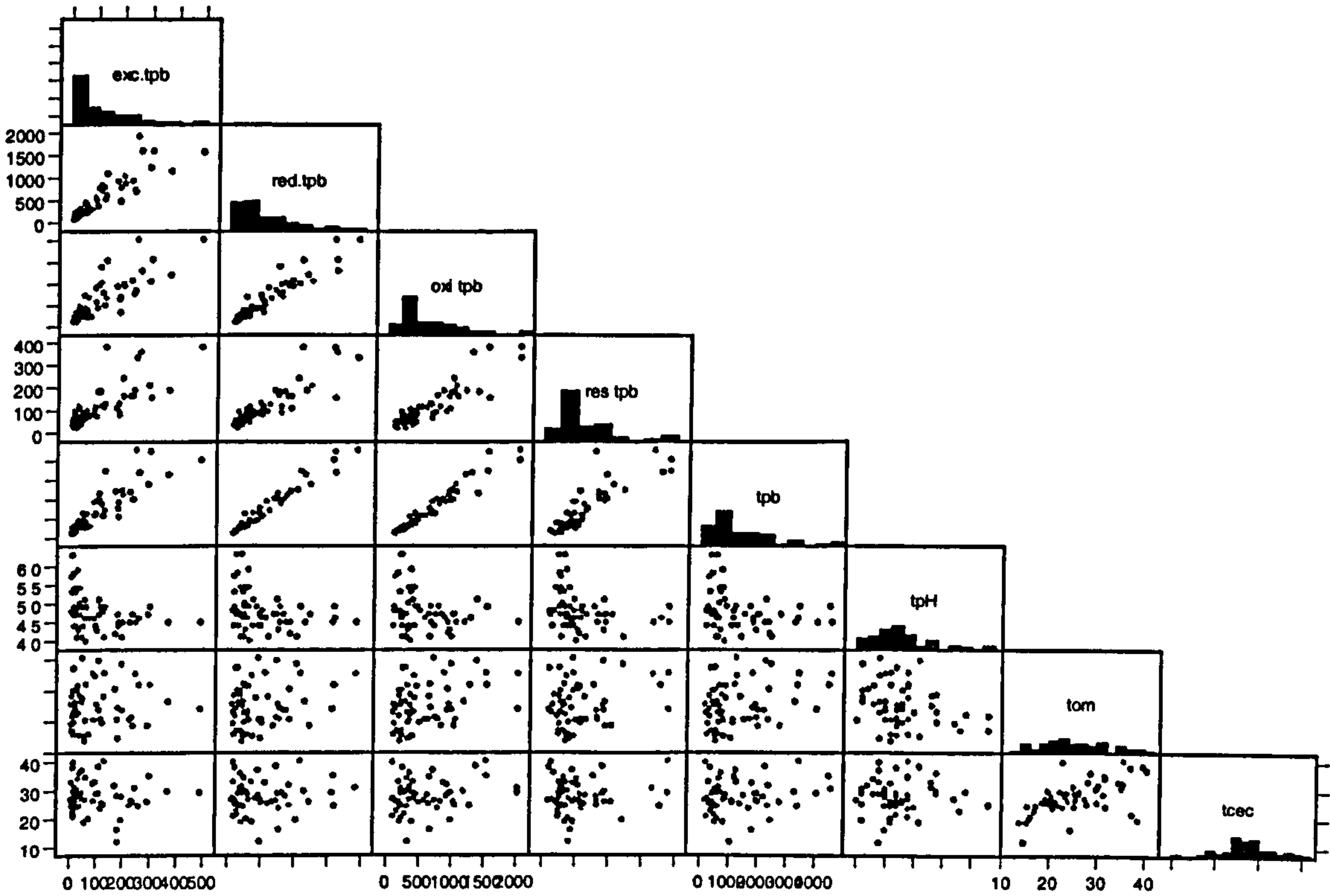


Figure 7.16 Scatter graph matrix depicting frequency distributions and associations between total Pb, Pb fractions and soil properties, top soil plot I

Correlation analysis also determined that certain Pb fractions exhibited significant associations with top soil pH, organic matter content and CEC, leading to the rejection of H_0 (Table 7.12). All displayed weak correlation coefficients $<|0.45|$ and a high degree of scatter (Figure 7.17). pH was significantly correlated with residual Pb ($p<0.05$), the negative coefficient indicating that a decrease in pH will lead to an increase in residual Pb concentration and therefore an increase in the more readily available fractions. Organic matter content was positively correlated with oxidisable ($p<0.001$) and total ($p<0.05$) Pb, a result of oxidisable Pb being bonded to organic matter. The oxidisable fraction has been shown to form a substantial proportion of total Pb (Figure 6.7). The significant correlation between organic matter content and CEC perhaps explains the positive association between oxidisable Pb and CEC ($p<0.05$), an increase in organic matter being known to increase soil CEC. Regression analysis determined that coefficients of determination, R^2 values, were low, the soil properties alone explaining a relatively low percentage of variation in fractional and total Pb concentrations (Figure 7.17).

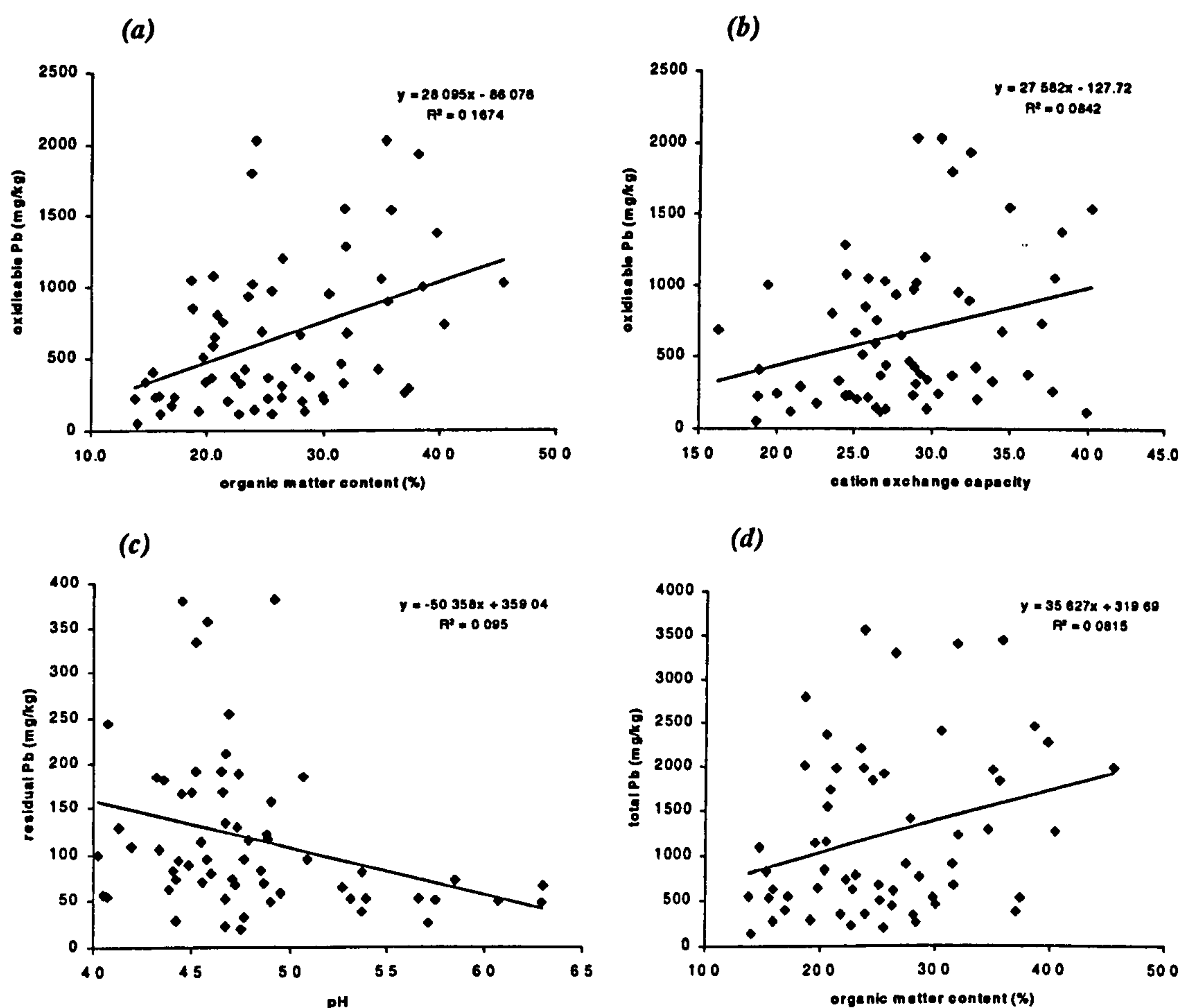


Figure 7.17 Relationship between top soil properties and Pb variables, plot I, (a) organic matter content and oxidisable Pb; (b) CEC and oxidisable Pb; (c) pH and residual Pb; (d) organic matter content and total Pb

Sub soil

PCA analysis identified a second cluster, also located at the negative end of the PC1 axis, that characterised the sub soil Pb variables (Figure 7.15). Again small angles of separation suggested, as expected, a high degree of correlation between the variables, the strengths of which were confirmed by correlation analysis. All associations exhibited moderate or strong correlations exceeding the 99.9% ($p<0.001$) critical value, hence the null hypothesis could be rejected with 99.9% certainty. All correlation coefficients exceeded 0.4500 (Table 7.13). Certain similarities were noted between associations in the top and sub soil layers. The relationships between total and reducible Pb and exchangeable and residual Pb displayed the highest and lowest correlation coefficients, respectively. In general, the scatter graphs depicted a low degree of scatter (Figure 7.18). All relationships exhibited positive correlation coefficients.

	exc-spb	red-spb	oxi-spb	res-spb	spb
exc-spb	1.000				
red-spb	0.8794*** (55)	1.000			
oxi-spb	0.7770*** (55)	0.8450*** (57)	1.000		
res-spb	0.4557*** (54)	0.6521*** (55)	0.7615*** (55)	1.000	
spb	0.8754*** (55)	0.9534*** (57)	0.9471*** (57)	0.6952*** (55)	1.000
sph	-0.3967** (52)	-0.3346* (53)	-0.2772* (55)	-0.1624 (53)	-0.3346* (57)
som	0.4863*** (56)	0.5153*** (55)	0.6507*** (57)	0.5645*** (55)	0.6131*** (55)
scec	0.2566 (56)	0.3450* (55)	0.3187* (57)	0.3822** (55)	0.3665** (55)

Table 7.13 Correlation coefficients for sub soil Pb, plot L

Clustering also determined that certain Zn fractions exhibited associations with sub soil properties, as indicated by the angles of separation on the PCA projection (Figure 7.15). All sub soil Pb fractions, except the residual, exhibited significant correlations with soil pH. All displayed correlation coefficients exceeding the 95% ($p<0.05$) critical value hence, H_0 could be rejected with 95% certainty (Table 7.13). Despite this, the fractions exhibited weak correlations with pH, scatter graphs exhibiting a high degree of scatter.

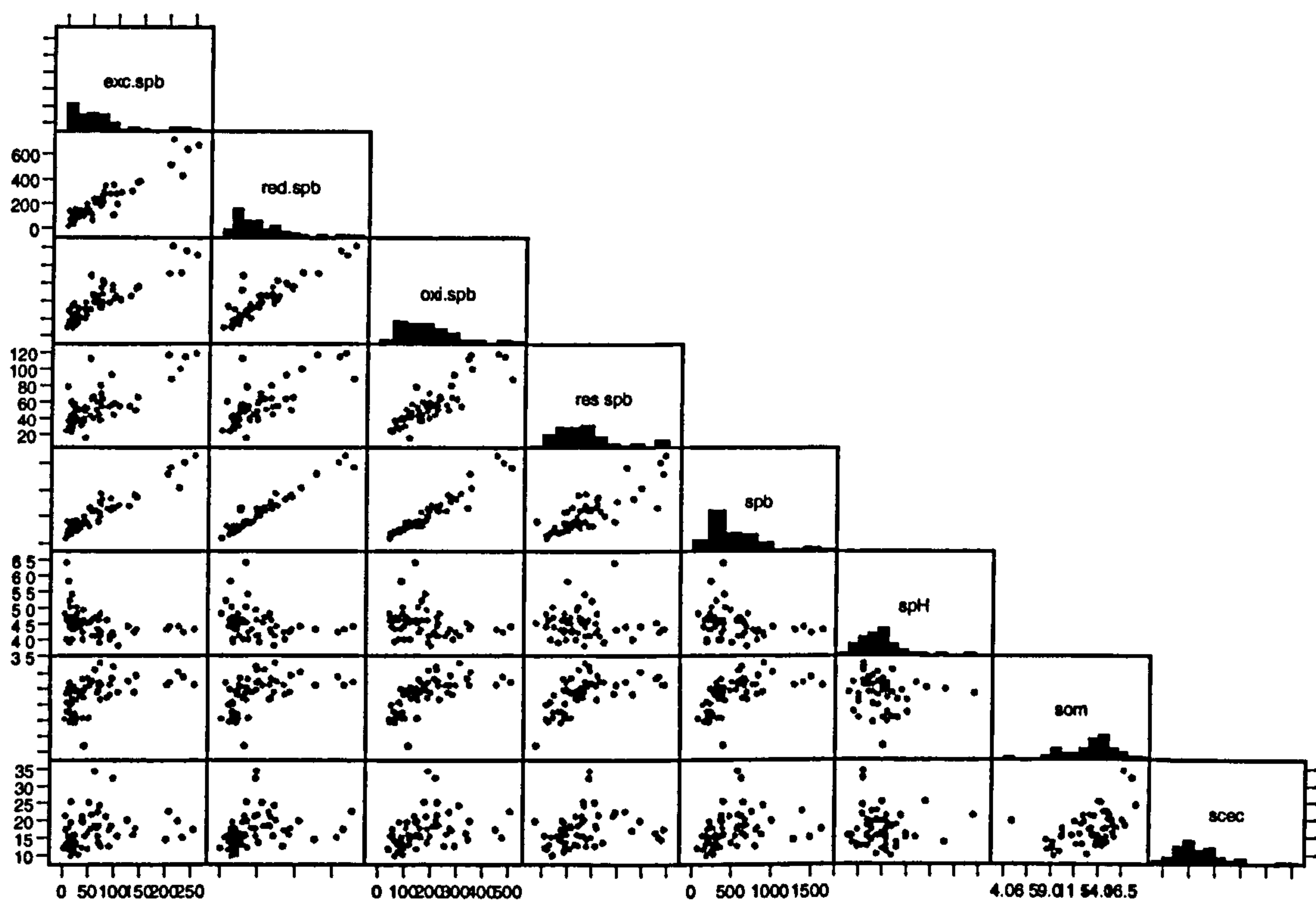


Figure 7.18 Scatter graph matrix depicting frequency distributions and associations between total Pb, Pb fractions and soil properties, sub soil plot I

All correlation coefficients were negative indicating that as soil pH decreased concentrations of Pb, in particular the potentially more mobile and available fractions, increased. Regression analysis determined that despite the significance of the associations, the percentage of variation in Pb concentration that was explained by variation in soil pH was relatively low. Soil pH best explained variations in the most readily available exchangeable Pb concentration although the R^2 value, approximately 16%, was relatively small. The equation of the regression line determined that a decrease of 1pH unit could lead to an increase of approximately 50mg/kg of exchangeable Pb within the soil (Figure 7.19).

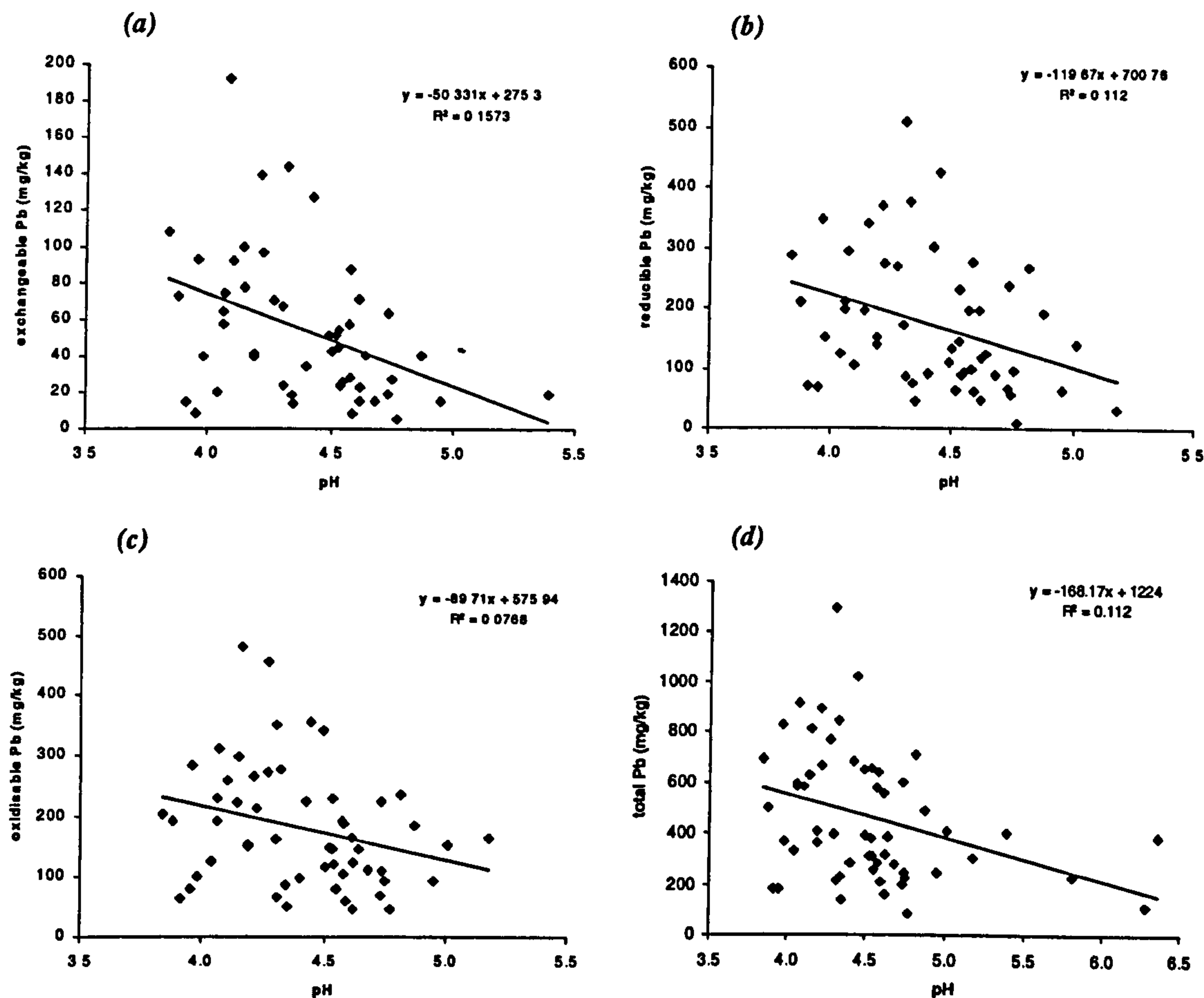


Figure 7.19 Relationship between sub soil pH and Pb variables, plot I, (a) exchangeable Pb; (b) reducible Pb; (c) oxidisable Pb; (d) total Pb

All five sub soil Pb variables displayed moderate positive associations with soil organic matter content. All correlation coefficients exceeded the 99.9% ($p < 0.001$) critical value, therefore, the null hypothesis could be rejected with 99.9% certainty (Table 7.13). The strength order of associations was of the order, oxidisable > total > residual > reducible > exchangeable. Regression analysis determined that variations in organic matter content explained relatively high proportions of the variation in sub soil Pb concentrations, far higher than within the top soil. It was noted that the percentage of organic matter within the sub soil was substantially lower than that within the top soil leading to the conclusion that type of organic matter may be more important than amount in the binding of soil Pb. The equation of the regression line determined that a 5% increase in sub soil organic matter content could lead to the retention of an extra 130mg/kg in the oxidisable form (Figure 7.20).

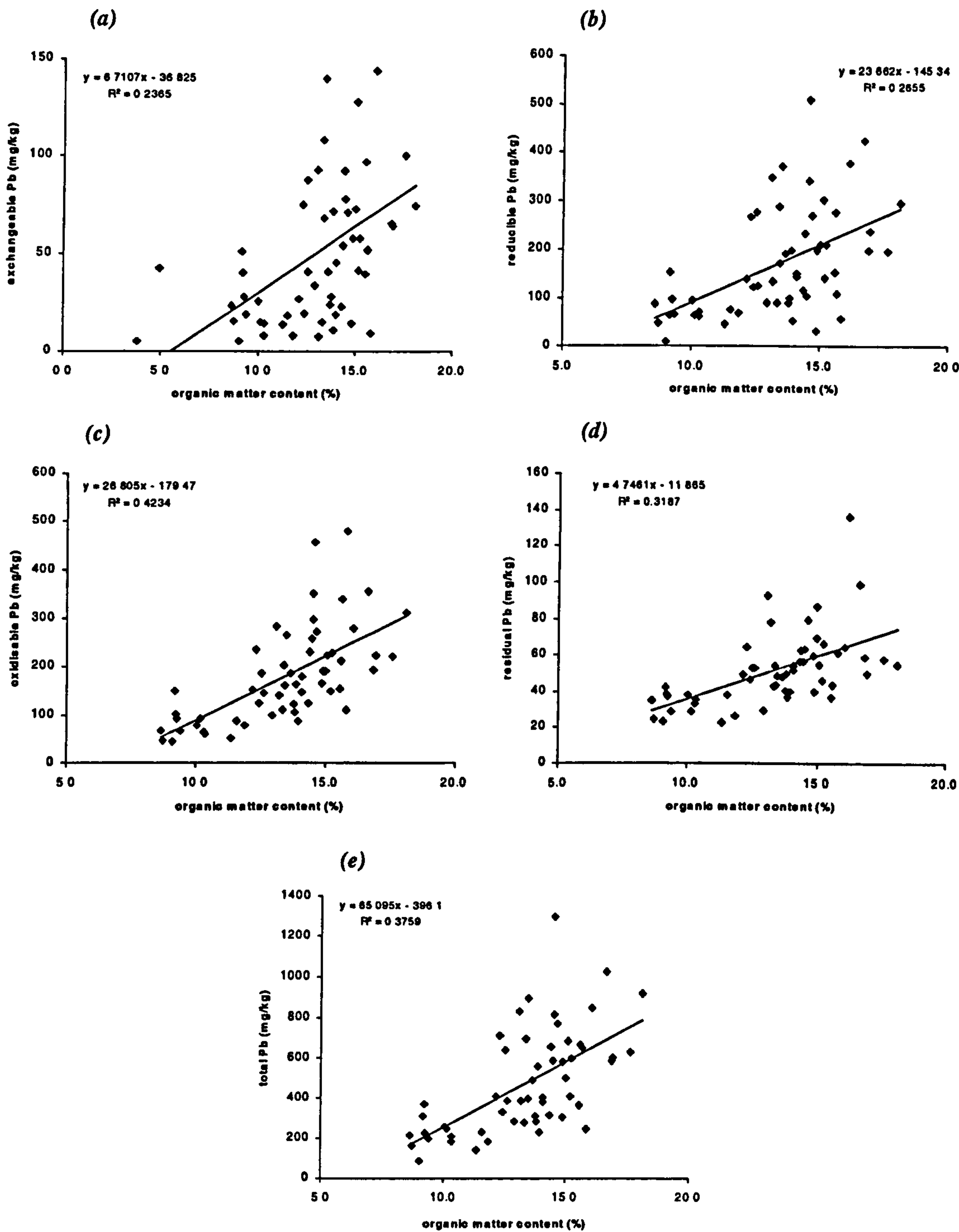


Figure 7.20 Relationship between sub soil organic matter content and Pb variables, plot I, (a) exchangeable Pb; (b) reducible Pb; (c) oxidisable Pb; (d) residual Pb; (e) total Pb

In contrast to the top soil, four out of the five sub soil Pb variables also displayed significant associations with CEC ($p > 0.05$). All coefficients were below $|0.45|$ and

hence the correlations classified as weak. The associations were positive, therefore, a higher soil CEC resulted in higher Pb retention. It was noted that the weakest association was with the oxidisable fraction despite this being the only fraction to display a significant association with CEC within the top soil. This result is thought to reflect different sources of CEC within the top and sub soil. Within the top soil CEC is strongly linked to organic matter although within the sub soil, where there is less organic matter; clay minerals play a more important role. R^2 values were low, variation in CEC explaining little of the variation in sub soil Pb concentrations (Figure 7.21).

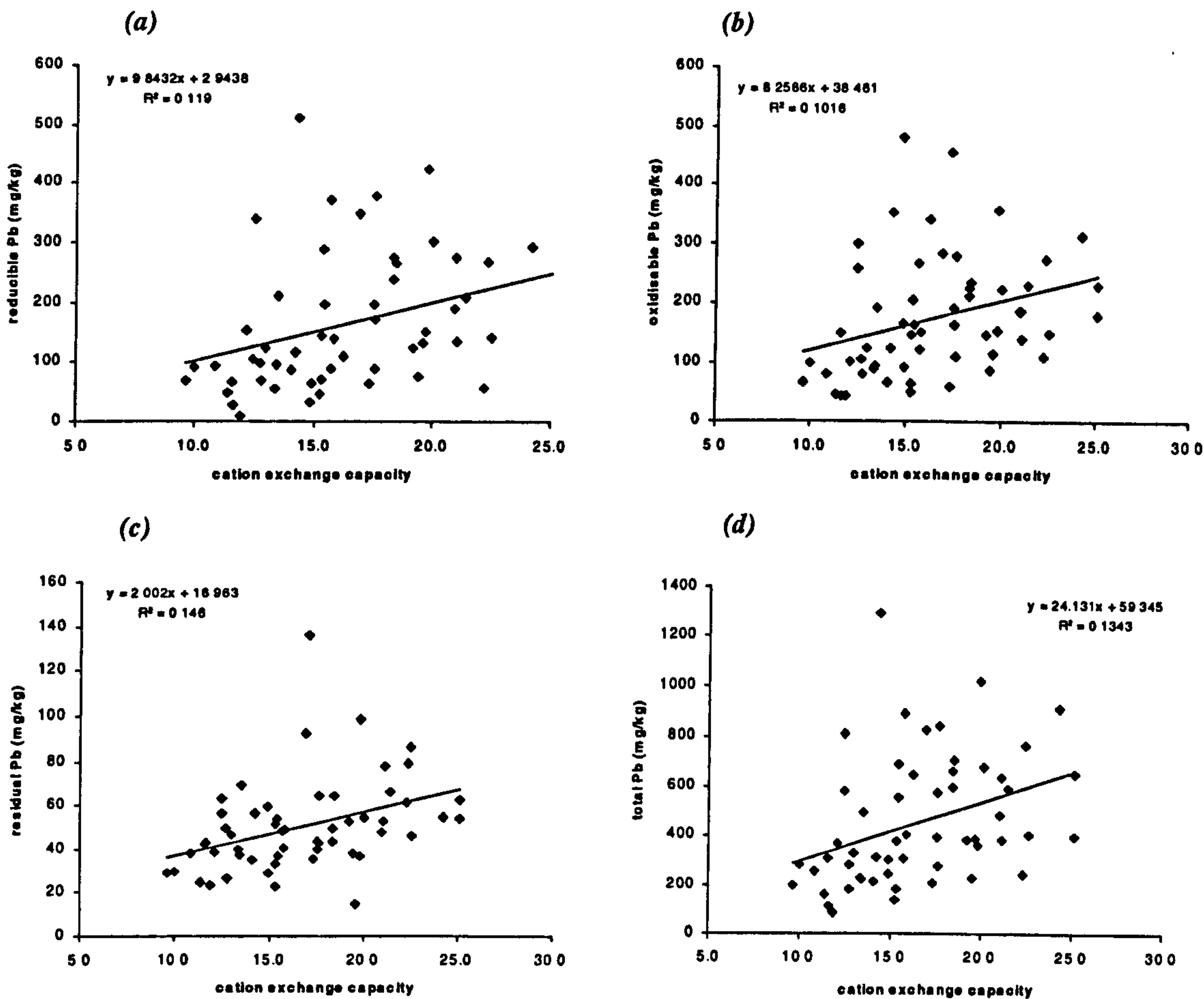


Figure 7.21 Relationship between sub soil CEC and Pb variables, plot I, (a) reducible Pb; (b) oxidisable Pb; (c) residual Pb; (d) total Pb

Top and sub soil

The PCA projection identified a main cluster of variables located on the negative side of the PC1 axis. This cluster was characterised by top and sub soil Pb variables, with small angles of separation indicating possible associations (Figure 7.15). Correlation analysis confirmed associations, of varying significance, between the corresponding Pb fractions within the two soil layers that, with the exception of the oxidisable fraction, led to the rejection of the null hypothesis (Table 7.14). A moderate correlation of 99.9% ($p<0.001$) significance was seen between the top and sub soil exchangeable fractions, thought possibly to reflect movement of the fraction down the soil profile. The association between top and sub soil total Pb was also found to be significant at the 99.9% ($p<0.001$) level. In addition, the top and sub soil reducible and residual fractions were significant at the 99% ($p<0.01$) and 95% ($p<0.05$) levels, respectively, exhibiting weak correlations. Associations were therefore of the order exchangeable > total > reducible > residual. Regression analysis determined that levels of explanation were variable, being greatest for exchangeable Pb. The regression equation determined that an increase of 50mg/kg of exchangeable Pb within the top soil may result in an increase of >10mg/kg within the sub soil (Figure 7.22). This result suggests that, under circumstances of high top soil exchangeable Pb concentration, downward movement of Pb maybe problematic.

	exc-spb	red-spb	oxi-spb	res-spb	spb
exc-tpb	0.5044*** (55)				
red-tpb		0.4107** (56)			
oxi-tpb			0.2293 (59)		
res-tpb				0.3263* (54)	
tpb					0.4318** (55)

Table 7.14 Correlation coefficients for top and sub soil Pb

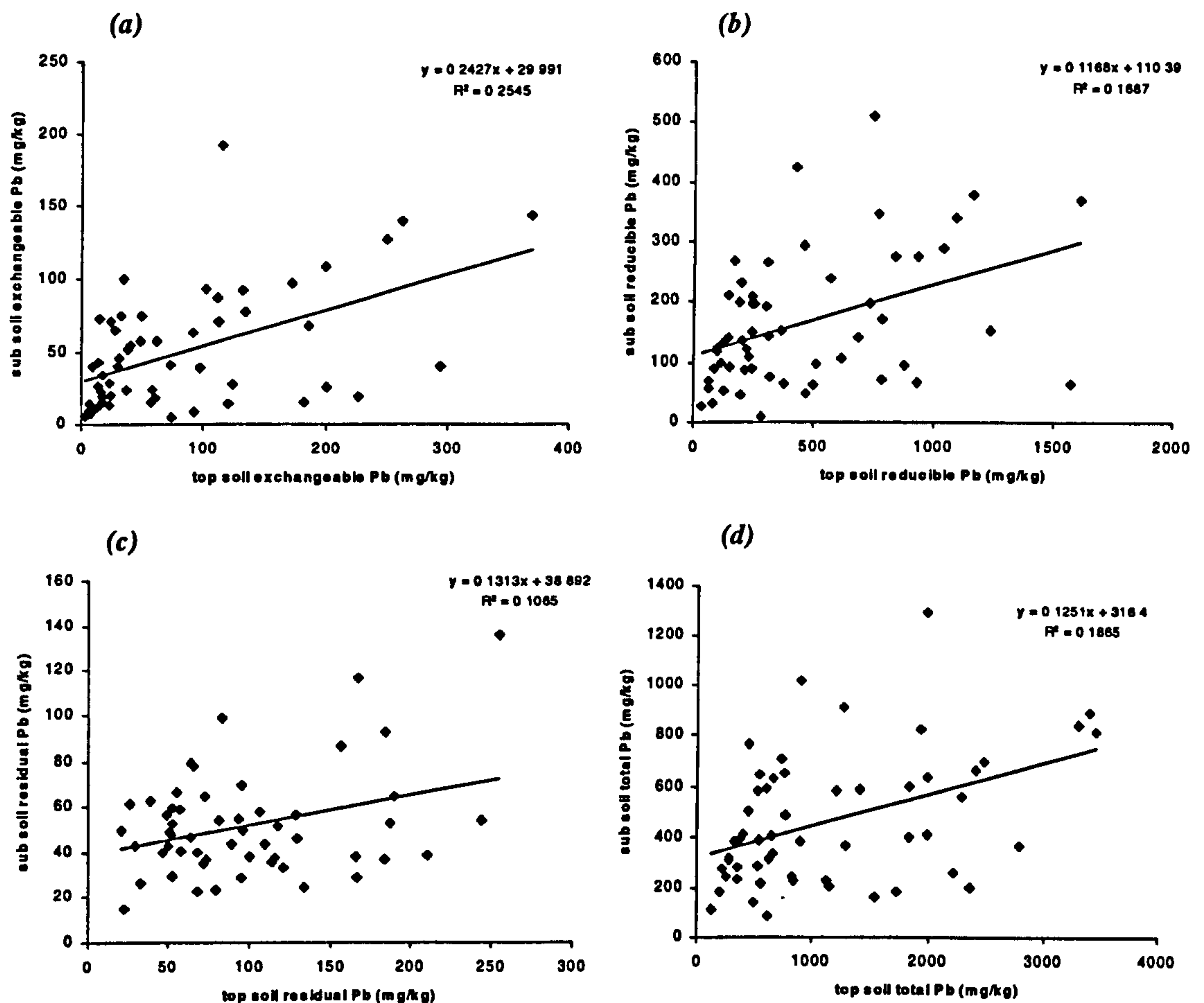


Figure 7.22 Relationship between top soil and sub soil Pb variables, plot I, (a) exchangeable Pb; (b) reducible Pb; (c) residual Pb; (d) total Pb

7.3.3.2 Zn

Top soil

PCA identified a cluster of top soil Zn variables located at the negative end of the PC2 axis, small angles of separation indicating that they may be inter-correlated (Figure 7.15). However, correlation analysis identified fewer and less significant associations between these top soil Zn variables in comparison to the top soil Pb variables. Seven out of a possible ten associations exhibited correlation coefficients in excess of the 95% ($p < 0.05$) critical value leading to the rejection of the null hypothesis. Four of these exceeded the 99.9% ($p < 0.001$) significance level, although only one correlation between total and exchangeable Zn could be classified as strong, the remaining three being of moderate strength (Table 7.15). In general, the strongest associations were between

total Zn and the Zn fractions. Scatter plots were noted as displaying a relatively high degree of scatter (Figure 7.23).

	exc-tzn	red-tzn	oxi-tzn	res-tzn	tzn
exc-tzn	1.000				
red-tzn	0.6516*** (61)	1.000			
oxi-tzn	0.3161* (62)	0.1965 (61)	1.000		
res-tzn	0.3262* (60)	0.2204 (59)	0.0336 (60)	1.000	
tzn	0.7587*** (59)	0.4809*** (61)	0.3174* (60)	0.6143*** (58)	1.000
tph	-0.0227 (56)	0.2218 (54)	0.1686 (56)	0.2142 (55)	0.2459 (54)
tom	0.6469*** (63)	0.4168*** (61)	0.4019** (62)	-0.1359 (60)	0.4763*** (59)
tcec	0.3912** (62)	0.2860* (58)	0.3900** (61)	-0.0260 (59)	0.3806** (58)

Table 7.15 Correlation coefficients for top soil Zn, plot I.

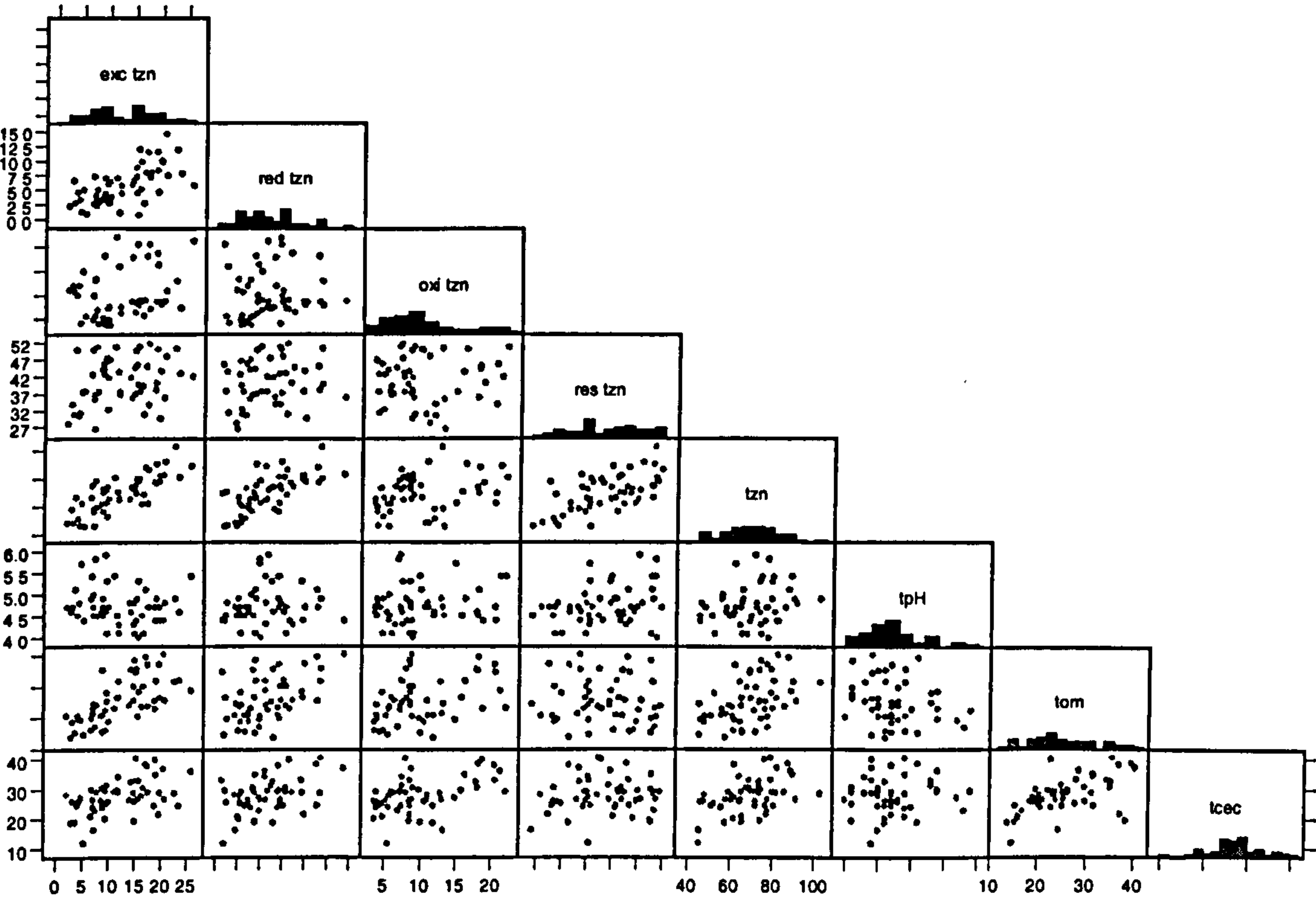


Figure 7.23 Scatter graph matrix depicting frequency distributions and associations between total Zn, Zn fractions and soil properties, top soil plot I

The PCA projection indicated that the majority of top soil Zn variables were more closely associated with soil organic matter and CEC than soil pH (Figure7.15). Correlation analysis confirmed this, none of the Zn variables exhibiting significant associations with soil pH. All correlation coefficients fell below the 95% critical value hence H_0 was accepted. However, significant associations were noted between organic matter content, CEC and all top soil Zn variables except residual Zn. Correlation analysis determined that variables displayed positive associations with both soil properties, although only two associations, that of exchangeable Zn and total Zn with organic matter content could be classified as of moderate strength. All other correlations were weak. Organic matter is thought to provide exchange sites for the

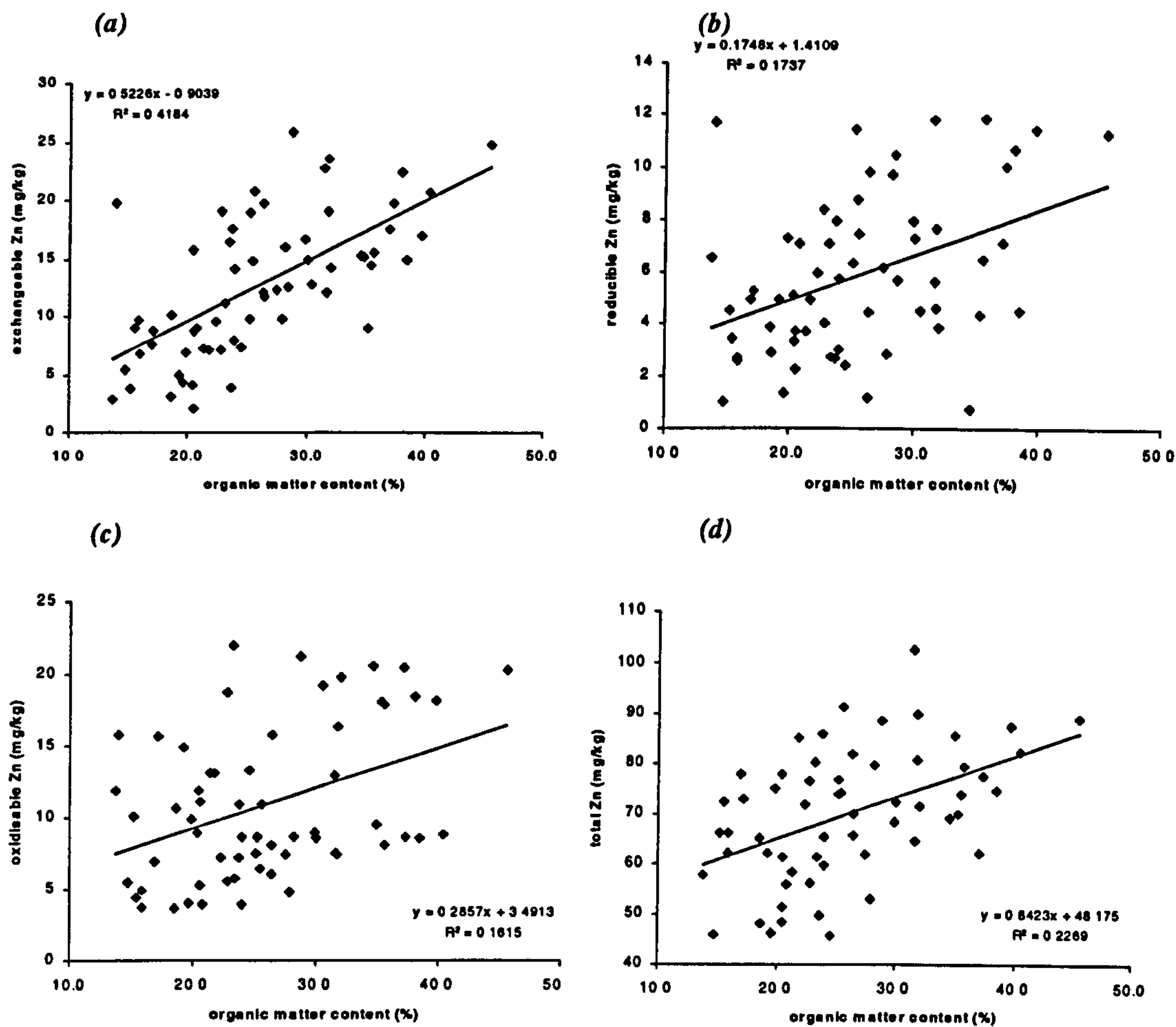


Figure 7.24 Relationship between top soil organic matter content and Zn variables, plot I, (a) exchangeable Pb; (b) reducible Pb; (c) oxidisable Pb; (d) total Pb

binding of exchangeable metal fractions, hence the positive association between the exchangeable fraction and organic matter content. The exchangeable fraction was also noted as displaying the strongest association with CEC. Levels of explanation, determined via regression analysis, varied dramatically for the different relationships (Figures 7.24 and 7.25). Regression equations determined that a 5% increase in organic matter content would lead to an increase of approximately 2.5mg/kg of exchangeable, readily available Zn, whilst an increase in CEC by 5me/100g would lead to an increase of 2mg/kg.

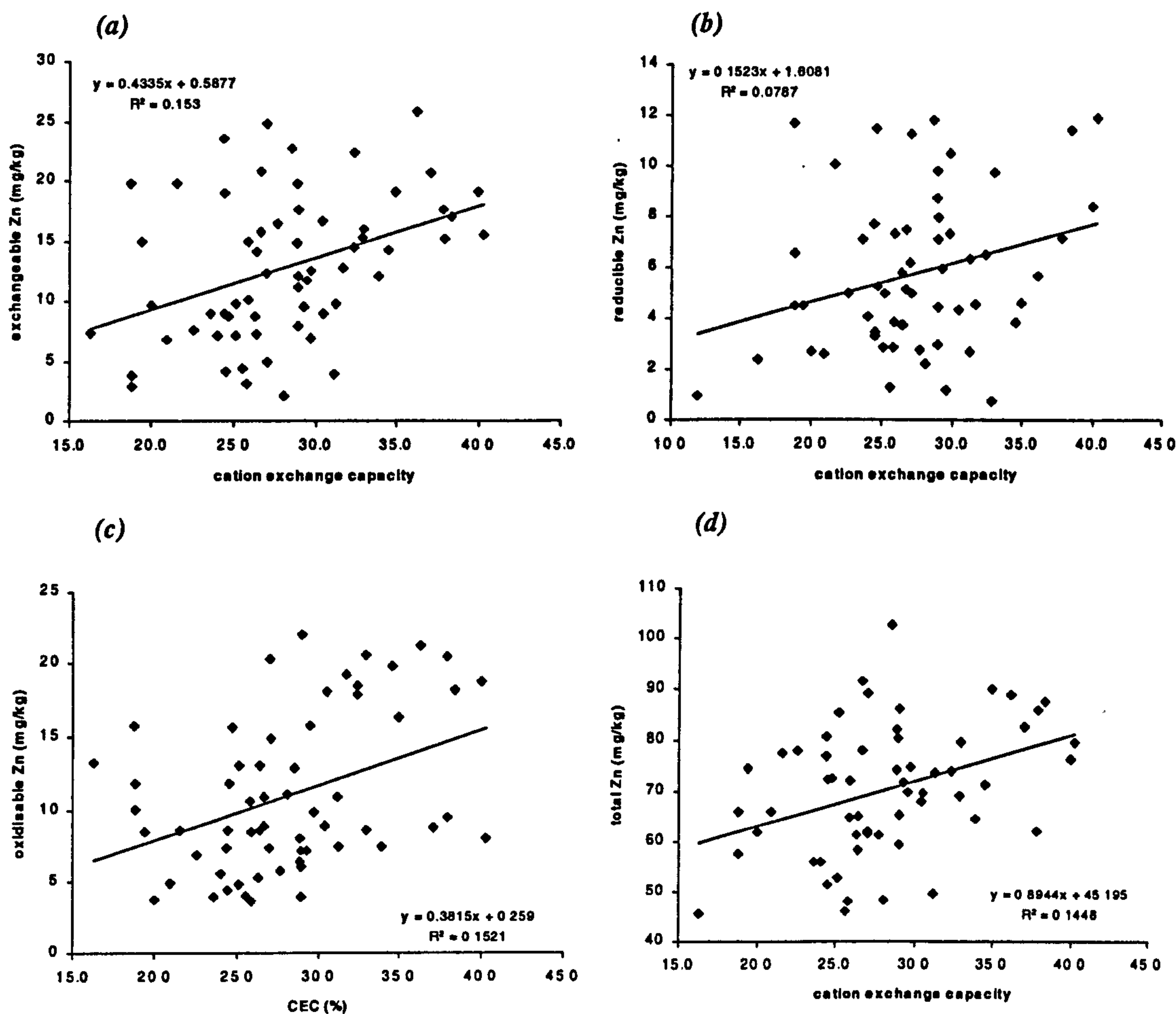


Figure 7.25 Relationship between top soil CEC and Zn variables, plot I, (a) exchangeable Pb; (b) reducible Pb; (c) oxidisable Pb; (d) total Pb

Sub soil

The PCA projection indicated a lower degree of clustering between the sub soil Zn variables (Figure 7.15). Despite this, correlation analysis determined that four out of the possible ten associations exhibited statistically significant correlation coefficients in excess of the 95% ($p<0.05$) critical value, leading to the rejection of the null hypothesis for these relationships. All four correlations were positive and weak, exhibiting coefficients $< |0.45|$. Fewer significant associations were noted between the sub soil Zn variables than the top soil Zn variables. Total Zn displayed significant associations with all Zn fractions except the reducible (Table 7.16, Figure 7.26).

	exc-szn	red-szn	oxi-szn	res-szn	szn
exc-szn	1.000				
red-szn	-0.0047 (56)	1.000			
oxi-szn	0.0752 (54)	0.0217 (59)	1.000		
res-szn	0.1587 (55)	0.3399** (60)	0.1365 (58)	1.000	
szn	0.3196* (55)	-0.0211 (60)	0.3743** (58)	0.4094** (59)	1.000
sph	0.1466 (53)	-0.0360 (59)	0.0489 (56)	0.0760 (57)	0.4256 (58)
som	-0.1313 (55)	-0.2751* (61)	-0.1260 (58)	-0.1614 (59)	0.0169 (59)
scec	0.1250 (54)	-0.0679 (59)	0.1834 (56)	0.0587 (57)	0.3467** (57)

Table 7.16 Correlation coefficients for sub soil Zn, plot I.

Fewer significant associations were seen between sub soil properties and Zn variables; note the high degree of scatter on the PCA projection (Figure 7.15). Weak associations were observed between pH, CEC and total Zn, leading to the rejection of the null hypothesis with 99.9 and 99% certainty, respectively. In contrast to Pb, total Zn was positively correlated with pH, hence higher concentrations of total Zn were seen in soils exhibiting higher pH. This result may reflect increased stability and reduced mobility of the metal under less acid conditions. In addition, reducible Zn was negatively correlated with organic matter, significant at the 95% ($p<0.05$) level. An increase in soil organic matter content was noted therefore as reducing concentrations of reducible Zn, indicating a possible preference of the metal to be bound in the oxidisable form. Despite this, no association was noted between oxidisable Zn and organic matter

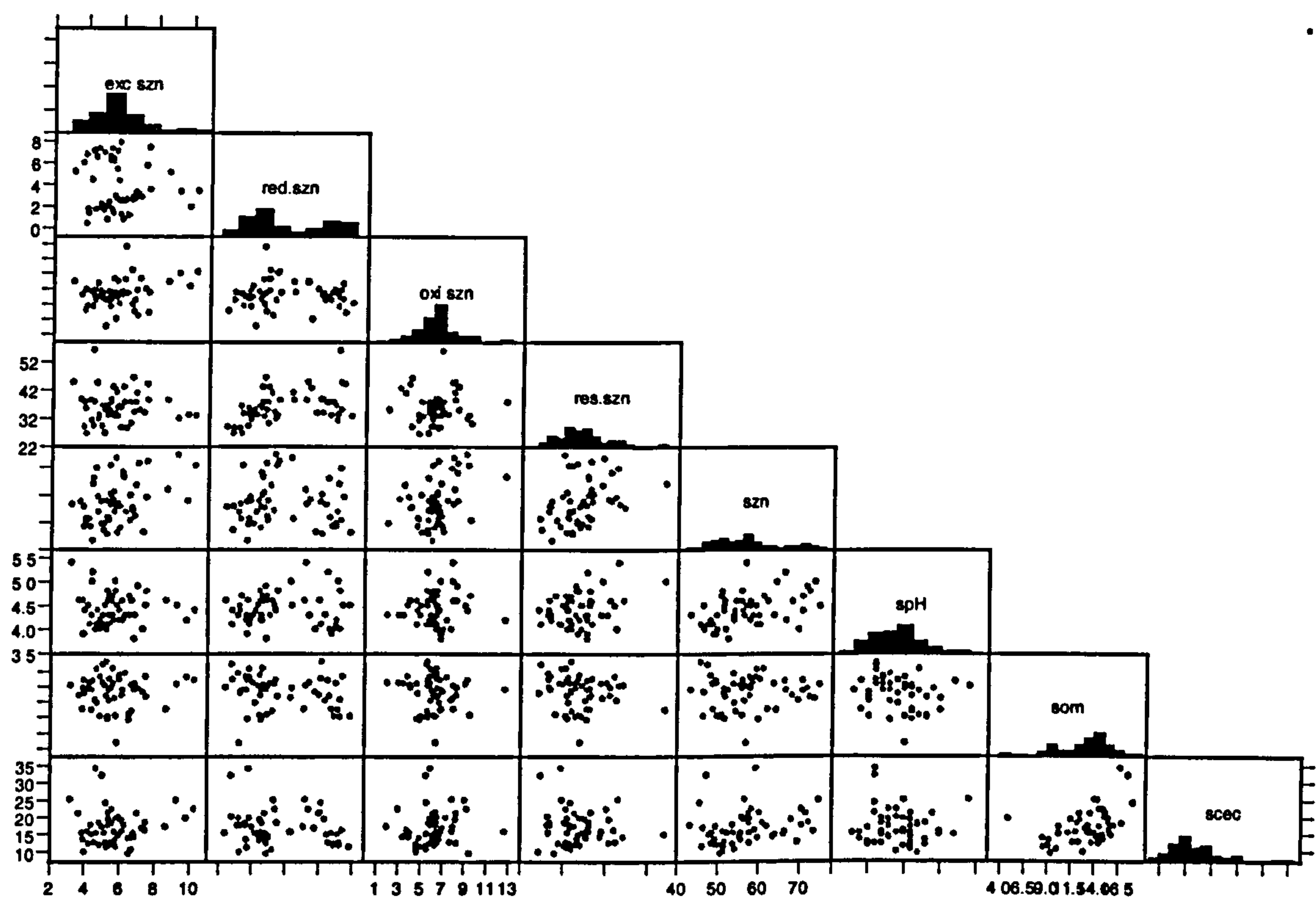


Figure 7.26 Scatter graph matrix depicting frequency distributions and associations between total Zn, Zn fractions and soil properties, sub soil plot I

content. Regression analysis determined that levels of explanation were relatively low (Figure 7.27).

Top and sub soil

The PCA projection displayed a high degree of scatter between top and sub soil Zn variables, although, correlation analysis indicated weak associations between two of the top and sub soil Zn variables, namely residual and total Zn (Figure 7.15). Both fractions exhibited positive associations leading to the rejection of the null hypothesis with 99% ($p<0.01$) and 99.9% ($p<0.001$) certainty, respectively (Table 7.17). The null hypothesis, of no association between variables, was accepted for the other three fractions. Regression analysis determined that levels of explanation were relatively low. Scatter graphs exhibited a wide scatter (Figure 7.28).

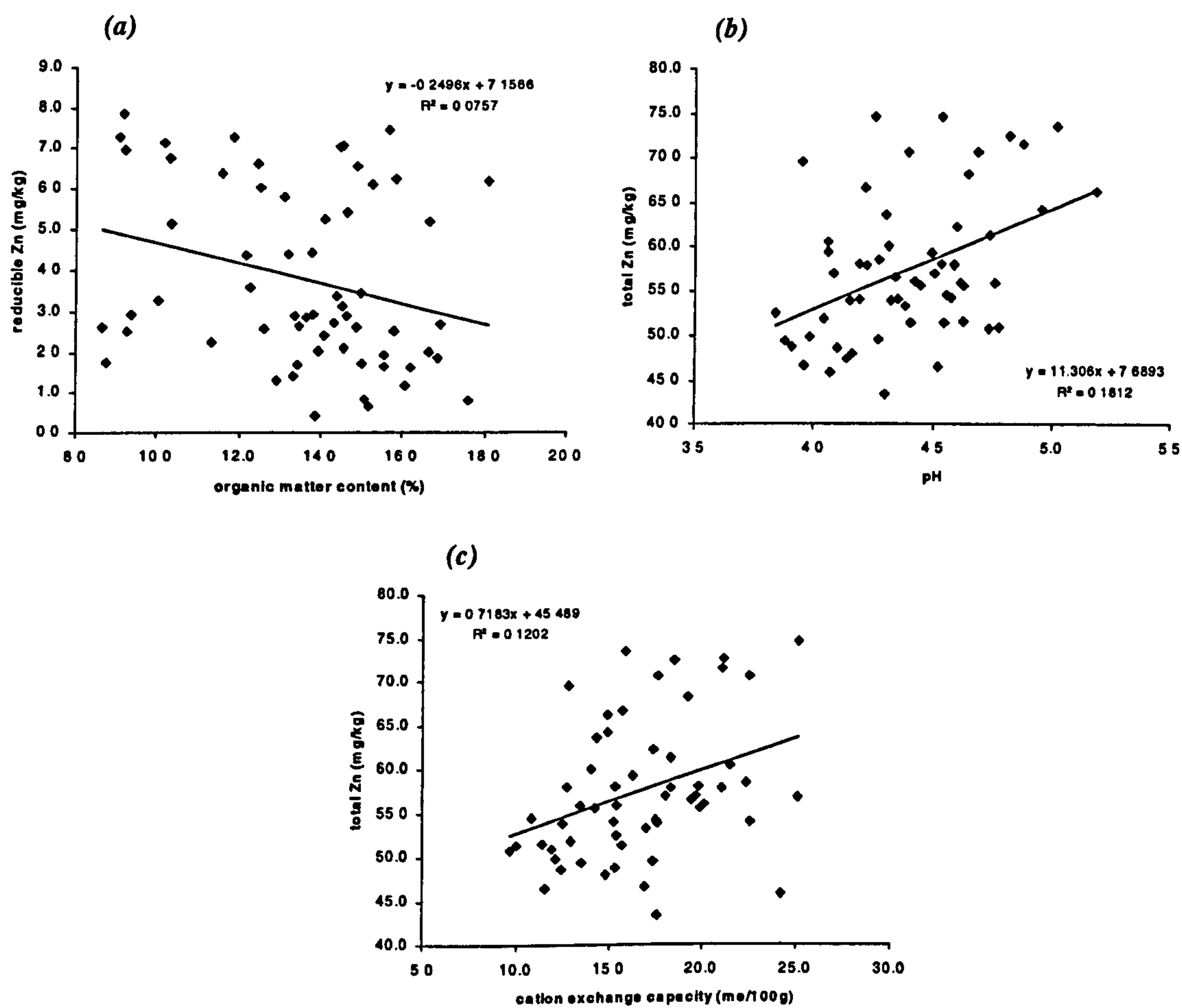


Figure 7.27 Relationship between sub soil properties and Zn variables, plot I, (a) organic matter and reducible Zn; (b) pH and total Zn; (c) CEC and total Zn

	exc-spb	red-spb	oxi-spb	res-spb	spb
exc-tpb	0.5044*** (55)				
red-tpb		0.4107** (56)			
oxi-tpb			0.2293 (59)		
res-tpb				0.3263* (54)	
tpb					0.4318** (55)

Table 7.17 Correlation coefficients for top and sub soil Pb

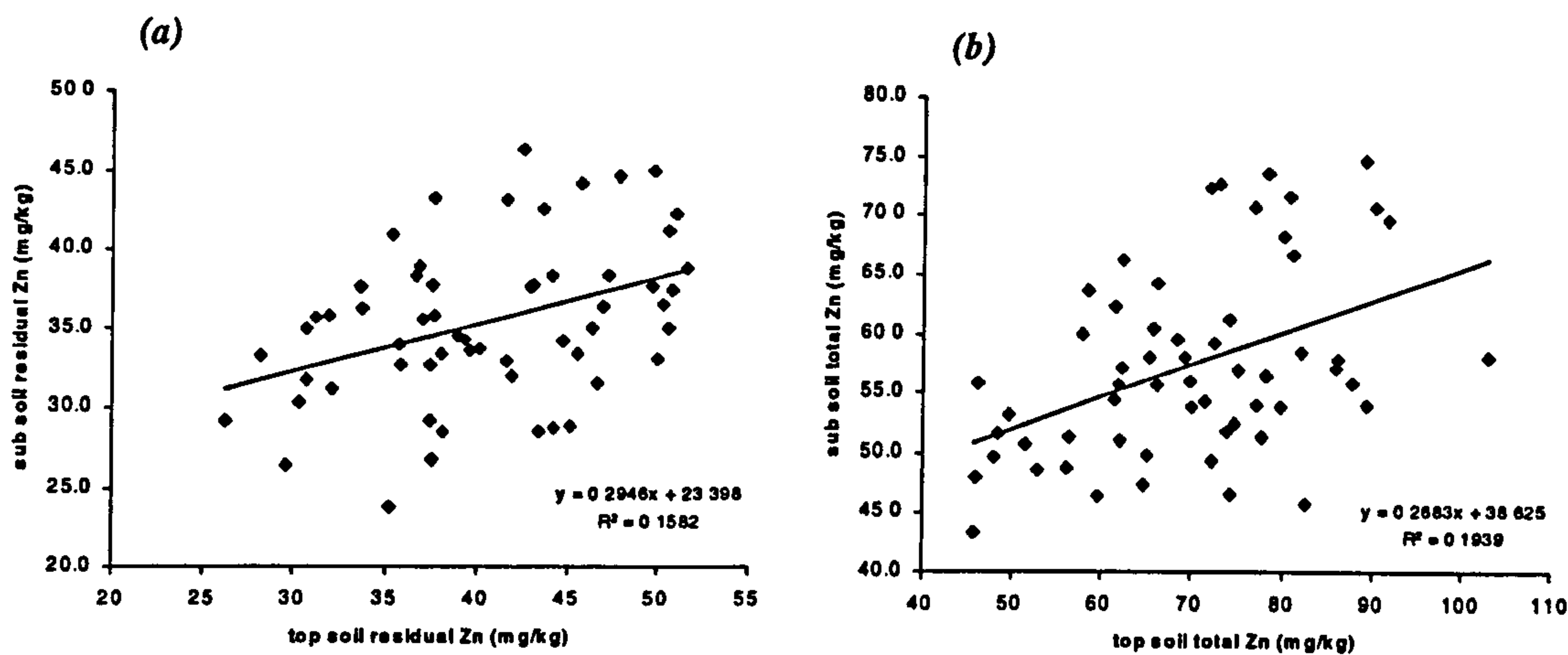


Figure 7.28 Relationship between top soil and sub soil Zn variables, plot I, (a) residual Pb; (b) total Pb

7.3.3.3 Pb and Zn

Correlation analysis determined only one significant association between the metals Pb and Zn within the soil of plot I. This association, between sub soil oxidisable Pb and Zn, significant at the 99% ($p < 0.01$) level, led to the rejection of the null hypothesis with 99% certainty (Table 7.18). The weak negative correlation between these variables suggests the possibility of some competition between metals for binding onto soil organic matter. Regression analysis determined that the level of explanation was low. The lack of significant associations between Pb and Zn points to separate sources of the two metals at the site (Figure 7.29).

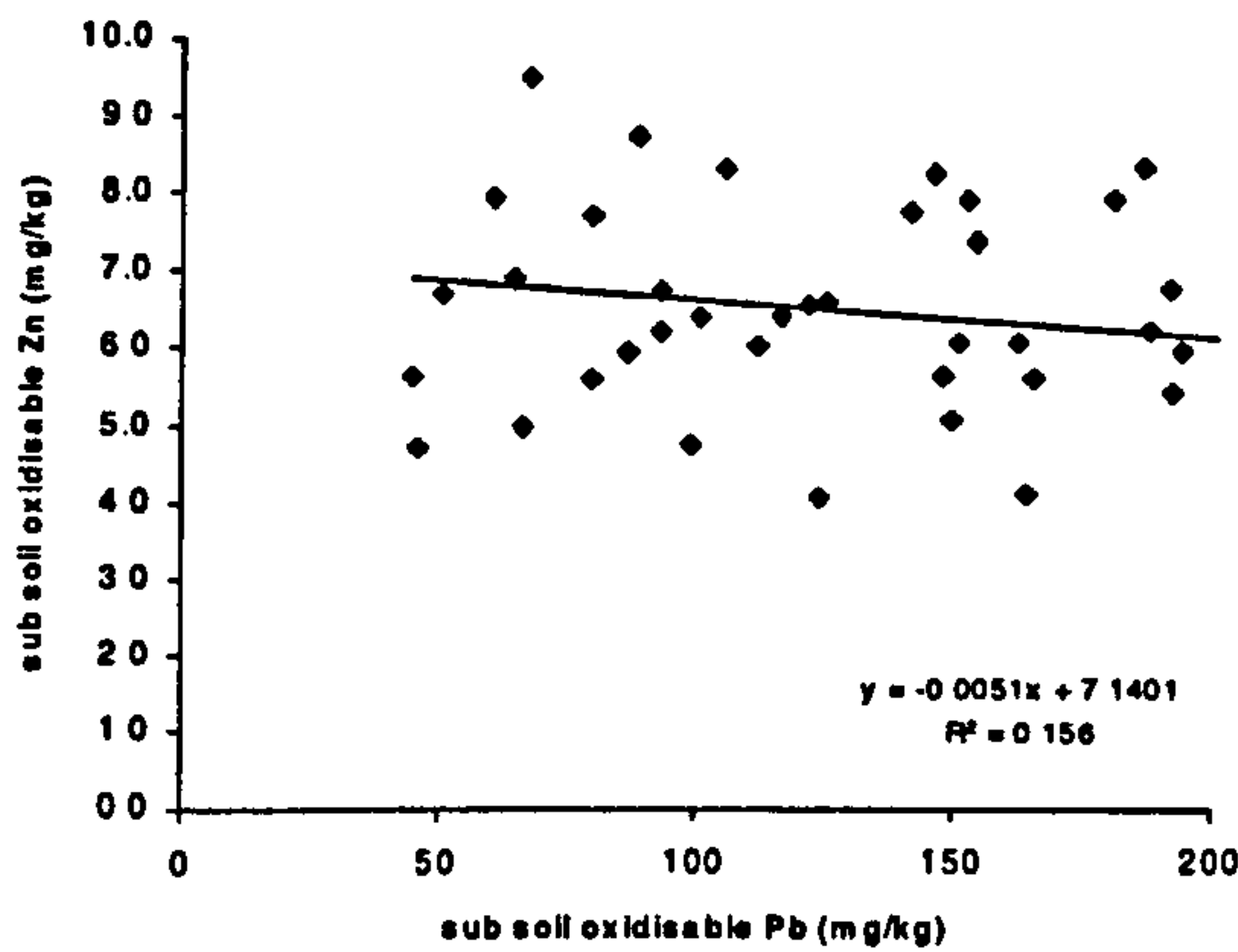


Figure 7.29 Relationship between sub soil oxidisable Pb and sub soil oxidisable Zn

	exc-tzn	red-tzn	oxi-tzn	res-tzn	tzn
exc-tpb	-0.1335 (62)				
red-tpb		-0.2437 (59)			
oxi-tpb			0.1287 (62)		
res-tpb				0.0112 (56)	
tpb					-0.1248 (56)
	exc-szn	red-szn	oxi-szn	res-szn	szn
exc-spb	-0.0642 (56)				
red-spb		-0.2191 (56)			
oxi-spb			-0.3950** (56)		
res-spb				0.0575 (57)	
spb					-0.0254 (54)

Table 7.18 Correlation coefficients for Pb and Zn fractions

7.4 SUMMARY

The soil properties, pH, organic matter content and CEC, were found to exhibit substantial variation within both the top and sub soil layers of plot I. Within the two layers pH was found to exhibit a similar mean and range, whereas organic matter content and CEC were lower within the sub soil. Correlation analysis determined that the soil properties exhibited statistically significant associations, with all three displaying relationships between the top and sub soil layers. In addition, CEC was closely related to organic matter content. Regression analysis determined that levels of explanation were relatively low, reflecting the high degree of scatter depicted by the scatter graphs.

PCA and correlation analysis identified a substantial number of associations between the variables measured within the top and sub soil layers of plot I. However, non-hierarchical cluster analysis failed to determine a single optimum classification when all variables were included in the analysis. Within both soil layers, the five Pb variables, exchangeable, reducible, oxidisable, residual and total Pb, were found to exhibit

positive associations statistically significant at the 99.9% ($p < 0.001$) level. In addition, associations were noted between Pb and these properties. Similar associations were seen between the two soil layers, although the sub soil Pb fractions exhibited more significant associations with pH than the top soil fractions. The oxidisable Pb fraction was found to be most strongly associated with organic matter content and CEC, within both soil layers. Significant associations were noted between like fractions within the top and sub soil layers. Regression analysis confirmed low levels of explanation (R^2 values) for these relationships.

The five Zn variables exhibited fewer and on the whole less significant associations than the Pb fractions, the top soil layer exhibiting seven out of a possible ten associations and the sub soil layer four. A similar number of associations were also noted between the Zn fractions and soil properties. Only sub soil total Zn exhibited a statistically significant association with soil pH. Organic matter content exhibited the largest number of associations with the Zn fractions, although these varied between the top and sub soil layers. The top soil Zn fractions displayed a number of associations with CEC, although only one significant relationship was noted with the sub soil Zn fractions. Two Zn variables, residual and total exhibited statistically significant associations between the top and sub soil layers. Again, regression analysis determined that levels of explanation were low, reflecting the high degree of scatter depicted by the scatter graphs. Few significant associations were noted between corresponding Pb and Zn fractions, total Pb and Zn concentrations exhibited no association.

CHAPTER 8

DISCUSSION

Summary

This chapter represents the main discussion of the thesis. It attempts to pull together and explain the main findings of the three results chapters (Chapters 5, 6, and 7), placing these in the context of existing literature. The chapter has been divided into 4 sections, which represent the main aims of the study (Section 1.2). Section 8.1, the introduction, explains how contaminated sites pose different levels of hazard, emphasising those populations and environmental systems most at risk. Section 8.2 discusses the variation in Pb and Zn contamination, looking specifically at concentration and spatial variation. Possible contamination sources are examined and attempts made to explain the patterns of variation. The issue of spatial complexity is raised and the usefulness of geostatistical techniques in a study of this nature discussed. Section 8.3 discusses the fractionation and behaviour of Pb and Zn, examining contaminant mobility and bioavailability, in addition to, the behaviour of Pb and Zn in relation to selected soil properties (pH, organic matter content, CEC). The section explains the importance of the exchangeable fraction, briefly evaluates sequential extraction techniques and investigates links between sources of metal contamination and partitioning. The relative hazard associated with any contamination is examined. Section 8.5 discusses the relative severity of Pb and Zn contamination in light of current legislative guideline values and 'trigger' thresholds, outlining the possible future prospects for metal contamination legislation. Recommendations for a new framework for assessment of heavy metal contaminated sites are made.

8.1 INTRODUCTION

Contaminated sites pose different levels of risk depending on both the nature and extent of contamination present at the site. In general, it is agreed that the degree of hazard associated with a site varies according to the physical form, composition of contaminants, quantities of contaminants, reactivity, biological and ecological toxicity effects, mobility in various environmental media, persistence and local site conditions (Kofi Asante-Duah, 1996). It has been noted that varying degrees of hazard may be associated with different contaminated site problems, with the mere existence of contaminated sites dictating that contaminant releases and exposures may occur. Acting as sinks, soils are recognised as potentially the most important primary sources of contaminant release to other environmental systems.

Current research has shown heavy metal contaminated soil to be a risk to human (Culbard *et al.*, 1988; Pirkle *et al.*, 1998; Mielke *et al.*, 1999), animal (Levy *et al.*, 1992), plant (Albasel and Cottenie, 1984; Martin and Bullock, 1994) and ecological (Martin and Bullock, 1994; Roane and Kellogg, 1996) health in addition to other environmental matrices, including water supplies (Flavin and Harris, 1991). Soil Pb enters the human body by direct ingestion and inhalation of soil particles and consumption of contaminated food and drinking water supplies, research having identified significant relationships between soil Pb and blood Pb concentrations (Mielke and Reagan, 1998). Studies have established a direct relationship between metal concentrations in plants and soil, although only a small fraction of total metal is available for plant root absorption (Davies *et al.*, 1987). In addition, animals are known to ingest significant quantities of soil particulates whilst grazing (Gupta *et al.*, 1996).

Within the soil, the behaviour of contaminants is controlled by a complex set of processes including transport, transformation, degradation, and biological uptake and bioaccumulation, making prediction of long-term behaviour difficult. Several factors contribute to the alteration of contaminant form, the soil, although a sink for many contaminants is not an inert repository. On the whole, solid phase contaminants are less susceptible to release and migration than fluids, the main forces behind soil contaminant transport being diffusive, with solubility affecting ultimate fate (Kofi Asante-Duah, 1996).

This chapter discusses the assessment and land management issues relevant to heavy metal contaminated sites. Initially, the discussion focuses on the variation in both heavy metal (Pb and Zn) concentration and spatial distribution, including the failure of coarse scale sampling to determine the true nature of contamination. Geostatistical techniques are critically evaluated for use within soil survey. The partitioning of Pb and Zn is examined within the soil of plot I, and the usefulness of sequential extraction techniques discussed. Top to sub soil enrichment ratios, are examined as possible indicators of contaminant availability, migration and source of heavy metals. The behaviour of Pb and Zn is discussed in relation to soil pH, organic matter content and CEC, providing indicators as to relative mobility, availability and potential hazard. Finally, the relative severity of any heavy metal contamination is discussed in relation

to current legislative guidelines and trigger thresholds, indicating changes necessary to move towards a more comprehensive system of hazard / risk assessment.

8.2 VARIATION OF HEAVY METAL (Pb AND Zn) CONTAMINATION

Heavy metal contaminants are often randomly distributed and heterogeneous exhibiting localised or hotspot patterns of spatial distribution (Isaacks and Srivastava, 1989). This raises problems regarding the interpretation of spatial patterns, prediction of contaminant location and distribution and identification of the extent of contamination. Sampling has been seen to fail in identification of the true nature of heavy metal distribution, often providing a simplistic view of contamination. Sampling density has been identified as affecting results (Kuzel *et al.*, 1994; Arrouays, *et al.*, 1996). However, the use of geostatistical techniques within soil science and land survey enables spatial information to be explored, conclusions to be drawn regarding the spatial continuity of variables and interpolation surfaces to be produced with a high degree of reliability. Such techniques may be used to determine where sampling density must be increased to enable prediction of contaminant levels to a certain degree of reliability (Webster and Oliver, 1990; Oliver and Webster, 1991).

8.2.1 Concentration variation

As expected, Pb and Zn concentrations were characterised by positively skewed frequency distributions, exhibiting many low and few high concentrations, a pattern which is often typical of geochemical data sets, particularly trace elements (Sections 5.2, 6.2 and 6.3). The positive skew is thought to result from the dilution effect of the dominant soil components on the minor components (e.g. trace metals), with the tail representing rare local occurrences of high concentrations. Similarly shaped distributions have been identified by numerous other investigations into soil heavy metal concentrations (Culbard *et al.*, 1988; Piostrowska *et al.*, 1994; Kelly *et al.*, 1996; Markus and McBratney, 1996; Pitchel *et al.*, 1997; Mellor and Bevan, 1999).

In general, the soil heavy metal concentrations were found to exhibit a wide range of values. Mean concentrations tended to be low, towards the bottom of the range, with high values present in only a small number of samples. Measures of central tendency

may be greatly affected by the outlying values of a skewed data set, the mean in particular becoming unrepresentatively high. The median is less affected by uncharacteristically high or low values. Use of the geometric mean has been suggested for the determination of central tendency when dealing with log normally distributed data sets, as this measure ensures that the few high values do not exert excessive influence on the characterisation of the distribution. If, however, as in this present study, the high values represent hot spot concentrations, the geometric mean will inappropriately discount these from the calculation. Non-inclusion of rare high concentrations may result in failure to identify potential risk to populations, particularly if spatial patterns dictate that areas of high concentration are in close proximity to a potential point of exposure. Potential points of exposure include, areas in close proximity to human populations, site access points, patches of bare soil, site boundaries which provide the potential to contaminate other sites previously classed as uncontaminated and areas in the vicinity of water courses. A number of these points of exposure are discussed later in relation to (a) the sites investigated and (b) the forms of Pb and Zn within the soil (Sections 8.23 and 8.31).

8.2.2 Spatial variation

The spatial variation of soil Pb and Zn concentrations was seen to exhibit localised patterns, with elevated concentrations often occurring in hot spot locations. This general pattern was noted at all sampling scales ($100 \times 100\text{m}$ – $0.5 \times 0.5\text{m}$) for Pb, although it was less marked for Zn, particularly at the finer scales (Sections 5.2, 6.2 and 6.3). Coarse scale sampling was therefore identified as failing to determine the true nature of Pb and Zn variation during this study. Pollutants were identified as being localised and patchy in their spatial distribution reflecting the two main pathways by which they reach the soil, deposition from air, either wet or dry, and / or the dumping of solid wastes (Holdgate, 1979). In surface soil, pollutants move relatively slowly and pathways tend to be short, movement being restricted to within percolating water or soil organisms. The inherent stability of Pb in relation to Zn perhaps explains the more patchy spatial distribution of Pb identified by the present study (Section 8.3.1). Radical differences in concentration and spatial distribution, in addition to a lack of correlation between the two metal concentrations suggests that the metals have arisen as the result of separate sources (Sections 8.3.2 and 8.4.3).

Similar hotspot patterns of soil heavy metal contamination have been identified by a number of studies conducted within urban environments in recent years (Douglas *et al.*, 1993; Kuzel *et al.*, 1994; Arrouays *et al.*, 1996; Kelly *et al.*, 1996; Markus and McBratney, 1996; Mellor and Bevan, 1999). Mellor and Bevan (1999) identified a very localised pattern of soil Pb contamination within the soils of public access areas within the Ouseburn catchment, Tyneside, the results of which are mirrored by this present investigation. Within urban environments, hot spots of heavy metal contamination have been associated with numerous anthropogenic activities, including major road networks (Douglas *et al.*, 1993; Kelly *et al.*, 1996; Markus and McBratney, 1996), past and present industrial activities (Kelly *et al.*, 1996), disposal of wastes from mining and chemical industries (Lin *et al.*, 1998), and metal smelting (Zachmann and Block, 1994).

8.2.3 Sites and possible sources

It was noted that spatial patterns and concentrations of total Pb and Zn within the top soil of the four sites (Town Moor, Nuns Moor, Hazelrigg nature reserve and South Gosforth) corresponded well with those identified by Mellor and Bevan (1999) and Aspinall *et al.* (1988), despite the different sampling scales (Section 5.2.2). All four sites exhibited higher concentrations of soil Pb than Zn, although some similarities in spatial distribution between the metals were noted.

Town Moor

Higher soil Pb concentrations were scattered across the Town Moor site although a cluster of samples displaying consistently higher concentrations was noted in the south eastern corner of the site (Section 5.2.2). This area of old common land is exposed to no direct industrial influences, but has in the past been used as a racecourse and golf course. Higher concentrations towards the eastern side of the moor are thought possibly to result from site disturbance and minor fuel spillages that may occur during the annual 'Hoppings' fun fair held on the site for two weeks during middle to late June (Mellor and Bevan, 1999). The moor is surrounded by main roads, including the busy A167(M) central motorway although, despite vehicular emissions being widely reported as a major source of urban Pb pollution (Albasel and Cottenie, 1984; Tiller *et al.*, 1987; Francek, 1992; Douglas *et al.*, 1993), they are not thought to contribute substantially to contamination at this site. Previous investigations have shown soil Pb

concentrations to decay exponentially with distance from roads with background levels being reached at less than 100m, a notably shorter distance than the present sampling site to the road. Tiller *et al.* (1987), however, suggested that approximately 3% of petrol derived Pb was dispersed beyond the immediate road zone, suggesting that pre introduction of unleaded petrol, vehicular emissions may have contributed to the higher than background concentrations of Pb at the site. The highest soil Zn concentrations were seen on the northern boundary of the site, although these bore no relation to the higher Pb concentrations. No obvious source could be identified for this Zn contamination.

Metal concentrations at this site did not exceed the British ICRL guidelines for allowable levels in the soil of parks, playing fields and open access areas, however it is thought that certain uses of this site could result in potential risk to human and animal populations. During the annual 'Hoppings' fun fair the grass to the east is exposed to a notable degree of wear often resulting in exposure of bare soil, which during a dry season results in the generation of substantial amounts of dust. The numerous visitors to this popular attraction may readily inhale this dust, with children thought to be most at risk, their bodies known to accumulate substantially higher concentrations of Pb than adults (Section 2.2). Cattle grazed on the Town Moor during this time will ingest the dust also settling out on the vegetation. It has been noted that plants take up metals from the soil (Section 8.3.2), hence the day to day grazing of cattle at this site may lead to metals entering the food chain. Once within the body, the metals may accumulate, be passed into the milk or excreted. Passing of metals through the animal digestion system has the potential to change the forms and hence availability and mobility of the contaminants in addition to redistributing them across the surface of the site.

Nuns Moor

Sampling on Nuns Moor indicated that an area approximately 100m by 200m was contaminated with Pb, although Zn concentrations were found to be low across the whole site (Section 5.2.2). The site, an area of ancient common land, exhibits ridge and furrow micro-topography suggesting agricultural use, although over the past 700 years a number of local disturbances have occurred within the adjacent areas. These include coal mining from the 17th century, sandstone quarrying until the 1950s and a

landfill site. South of the site and covering a substantial proportion of Nuns Moor is Newcastle golf course. There are no major roads within the vicinity of the sample site.

The Golf course, requiring frequent applications of both pesticides and fertilisers in order to maintain grass quality under the stressful conditions produced by heavy usage, has been considered as a possible source of heavy metal contaminants at the site. For example, pesticides, herbicides and fertilisers have been identified as the three main sources of Pb pollution within northern Jordan (Abu-Rukah, 1998) with the past use of lead arsenate insecticides thought to elevate concentrations of both Pb and As in top soils (Peryea and Kammereck, 1997). The highest concentrations of Pb and Zn have been identified within herbicides and copper sulphate and iron sulphate fertilisers (Gimeno-Garcia *et al.*, 1996). Phosphate fertilisers are also known as a source of Pb, As and Cd, the original phosphate rock containing relatively high concentrations of these elements (Fergusson, 1990). The need for pesticide treatments is intensified as golf course turf usually consists of only one or two grass species, allowing disease to thrive. During application, whether in solid or liquid form, pesticides and fertilisers are emitted into the atmosphere, where transportation potential depends on their ability to be mobilised by the air, and on the removal processes (wet and dry deposition) that take place. The distance and direction over which such sprayed chemicals will be carried depends on a number of factors, such as wind velocity, prevailing wind direction, temperature and particle density. The prevailing wind direction in Tyneside, approximately westerly, points to aerial deposition of heavy metal containing agrochemicals used during the maintenance of Newcastle golf course as a possible source of soil Pb contamination at the Nuns Moor site. The possible use of the area as agricultural land indicates that fertilisers and pesticides may have been applied directly to the site in the past. The site is occasionally used by children for trail biking from which minor fuel spillages may lead to very localised patches of soil contamination, although it is unlikely that contamination of this scale will be identified by the present sampling regime (100 × 100m).

Although on average soil Pb concentrations at this site did not exceed the British ICRCL guideline for public access land, the survey has, in the form of individual samples, raised concerns for both human and animal health. Certain samples have

been identified as exceeding the 2000mg/kg limit, hence indicating a possible need for soil reclamation within this area. As with the Town Moor, the Nuns Moor is used for the grazing of cattle for approximately 6 months of the year, hence this raises concerns regarding the possible entering of Pb into the food chain. Grass Pb concentrations at this site were not examined during this study although previous research has identified relationships between exchangeable or EDTA extractable Pb and uptake by plants (Section 8.3.2). Although this fraction forms a relatively small percentage of soil total Pb, high concentrations of total Pb can lead to relatively high concentrations of the exchangeable fraction (Section 6.2.1). Further research would be required to establish the degree of plant Pb uptake at this site. Animals are also known to ingest significant quantities of soil particles during grazing, hence there exists the potential for Pb to enter the food chain in this manner.

During the summer months several patches of bare soil were noted at this site, mainly in the vicinity of the footpaths and the watercourse running along the northern boundary of the site. These patches are thought to result from use of the area for trail biking in addition to being areas where the cattle accumulate to drink. As previously stated exposure of the soil increases the risks associated with contaminated soil as in dry weather, particularly during heavy usage, dust is created. The problems associated with dust namely inhalation and settling out on nearby vegetation have previously been stated. It was noted that gardens, housing and a school playing field adjacent to this site may be at risk of contamination by dust particles, increasing potential risks to human, particularly children's, health. Any dust deposited in the watercourse has the potential to affect aquatic life not only within the local area but the river Ouseburn of which it is a tributary.

Hazelrigg nature reserve

The Hazelrigg nature reserve, the most rural of sites investigated, exhibited the lowest and least variable soil Pb concentrations. However, the site, a reclaimed colliery spoil tip, did exhibit a number of samples displaying higher (>100mg/kg) concentrations of both Pb and Zn (Section 5.2.2). Pb and Zn in colliery spoil are thought to be derived from pyritic shales (Prade *et al.*, 1991), the oxidisation of which releases heavy metals. These shales form a significant part of the coal bearing geology of north-central Newcastle (Mellor and Bevan, 1999), and therefore a possible source of the slightly

elevated patches of soil Pb and Zn concentrations at the Hazelrigg site. Teixeira *et al.*, (1999) identified significant concentrations of total, leachable and soluble Pb and Zn in residues from coal processing, the elements being associated with sulphides, sulphates and organic matter in coal. The Hazelrigg site has only recently been reclaimed and covered with imported top soil.

It was noted that the higher Pb and Zn concentrations were seen in the north of the reserve often adjacent to the footpaths covered by coal spoil. Concentrations were however a factor of ten times lower than the ICRCL guidelines. These areas are the most heavily used by the public hence their contamination poses a potentially greater risk associated with increased likelihood of exposure. On the whole, areas immediately adjacent to footpaths are likely to be subject to a higher degree of disturbance and wear, hence it is possible that top soil within their vicinity may be thinner or absent. Spoil from the paths may also have been disturbed by the action of walking and cycling, forming dust which is most likely to be deposited within the immediate vicinity, thus contaminating nearby soils. Moreover, any dust is available for human and animal inhalation prior to settling. Again, the deposition of contaminated dust on vegetation is liable to increase concentrations of metals within plants. Other heavy metal contaminated hot spots were associated with a thinner layer or absence of top soil.

The Hazelrigg site is drained by series of ditches or small channels in addition to a number of surface water bodies. These water bodies, located on the western side of the site, are relatively extensive during the wetter winter months, although are notably reduced in size during the summer. The clayey top soil, imported to cover the coal spoil, acts as a barrier to drainage allowing water to accumulate on the surface. Water logging of the soil in the vicinity of these water bodies provides the potential for changes in metallic form and hence changes in the availability and mobility of any metals (Section 8.3.6). Concentrations of dissolved Pb and Zn were not examined in these water bodies, although due to the low soil metal concentrations and the relatively insoluble nature of Pb and Zn within water, concentrations were thought to be low. Further analysis would enable either the confirmation or refutation of this hypothesis and hence the level of risk associated with water draining from this site to be determined. Any risks may be associated with the health of aquatic life, potential

contamination of other sites, contamination of ground water due to movement of water down the soil profile in addition to, potential affects on human health as a result of contact with the water.

South Gosforth

In general, the South Gosforth site exhibited relatively low soil Pb and Zn concentrations, although concentrations of Pb did exceed the background level for Tyneside specified by Aspinall *et al.* (1988). Again, localised contamination was noted with a single sample containing >5000mg/kg and >1300mg/kg of Pb and Zn, respectively (Section 5.2.2). This sample far exceeded the 2000mg/kg ICRCL guideline for Pb within the soil of parks, playing fields and open access areas, corresponding well with the results of Mellor and Bevan (1999). Such hotspot contamination is difficult to source, although aerial photographs taken in 1992 provide evidence of site disturbance within the area from which the sample was collected. Photographs reveal an area of dead grass, perhaps the site of a bonfire. This grass had regenerated prior to the site investigation leaving no outward signs of disturbance (Plate 3.9). It is possible therefore that the patch of contamination identified at the site is the result of something put on the fire, for example a battery. Small sealed household Pb batteries have been identified as a major source of Pb in household waste, the incineration of which leads to the transfer of 33% of the Pb to fly ash (Nakamura *et al.*, 1996).

This small grassland site is an important resource for local residents as the majority of houses in this area have little or no garden. The site is a well used play area for local children, hence high levels of soil contamination are of particular concern. In addition to children accumulating higher proportions of Pb within their bodies the nature of their play increases the likelihood of exposure to contaminated soil. The site has, in general, been identified as exhibiting both Pb and Zn concentrations well below specified guideline levels for its land use, however a hot spot of contaminated soil was found. The actual risk associated with this hot spot is difficult to quantify although, as the contaminated spot is small (adjacent samples exhibited metal concentrations inline with the rest of the site) and the site well vegetated, exposure seems unlikely. The cost of remediating such a site on the basis of the identification a single small hotspot of contamination is thought to exceed any risk posed.

8.2.4 Complexity of spatial distribution

Assessment of samples collected at four different scales ($100 \times 100\text{m}$, $25 \times 25\text{m}$, $5 \times 5\text{m}$, $0.5 \times 0.5\text{m}$) within the Nuns Moor site highlighted the complexity of soil heavy metal, particularly Pb, contamination. Complex hot spot patterns of spatial distribution were identified at each sampling scale, with concentration variation at the finest scale as great if not greater than at the coarsest scale (Sections 5.2.2 and 5.2.3). The results, highlighting the variability of heavy metals within soil, mirrored those of Kuzel *et al.* (1994) who identified elevated micro-regions of Cd contamination when sampling at two different scales ($100 \times 100\text{m}$ and $10 \times 10\text{m}$). The high spatial variability of soil metal content strongly limits the objective assessment of pollution severity, spatial sampling density being known to affect the results of site investigations (Mellor and Bevan, 1999). Coarse scale sampling networks can fail to identify the true nature of contamination, although sampling at an inappropriate spatial frequency may result in samples being non-representative of contamination present at a site. Heavy metal contamination may be randomly distributed and heterogeneous.

Two types of spatial variation may be defined within soil, namely random and systematic. Systematic variation is a gradual or marked change in soil properties as a function of landforms, geometric elements, soil forming factors or soil management, whereas random variation describes differences that cannot be explained in terms of known soil factors or are not recognisable at a reasonable sampling density (Saldana *et al.*, 1998). Present research indicates that the spatial distribution of Pb and Zn concentrations within the soil of the Nuns Moor site may be considered as random. The point at which variation may be classed as random is difficult to define, although geostatistical methods are a useful tool for investigation of the character and spatial structure of pollution (Einax and Soldt, 1995).

Within the present study, differences in concentration were noted between corresponding samples of the four sampling scales. These differences were thought to result from a combination of factors, including, operator error (samples not being collected from exactly the same location), micro-scale variations in soil Pb concentration and within sample heterogeneity (Appendix 2).

8.2.5 Geostatistical analyses

Geostatistical analysis of soil Pb and Zn concentrations determined that a sampling frequency of $0.5 \times 0.5\text{m}$ was required before clearly structured, well-defined variograms could be produced and the spatial dependence (Appendix 5) of metal concentrations within the soil determined (Section 5.3). However, even at this fine sampling scale nugget variances were noted (Appendix 5). Nugget variances arise as the result of either (or a combination of) measurement error or the spatial dependence of a property occurring over a smaller distance than the shortest sampling interval. A large nugget variance may therefore indicate micro-scale variation of a property. Results of this present study are similar to those of Arrouays *et al.* (1996) who determined that Pb variation over 1m was of the same order as within a $40 \times 40\text{m}$ plot, concluding that the nugget effect was mainly due to micro-heterogeneity. Soil Pb concentrations at the Nuns Moor site varied dramatically from one micro-site to another making the monitoring of the element difficult.

The variogram calculated for total Pb within plot II ($5 \times 5\text{m}$ scale) was best fit by a purely nugget variogram (Figure 5.13) indicating a lack of spatial structure to Pb concentrations at this scale (flat variograms are typical of random variation). This result reflects that of Woperies *et al.* (1998) who identified no spatial structure when examining Pb and Zn concentrations within a 1ha plot. Other studies have identified varying levels of spatial dependence for heavy metals within soil and sediments, ranging from several kilometres (Tao, 1995) to a few meters (Boekhold and Van der Zee, 1992; Kuzel *et al.*, 1995). Amalgamation of the Nuns Moor data sets, from (1) the top and sub soil of plot I and (2) all three plots, failed to improve the structure of the variograms at the site. Poorly structured variograms were not therefore thought to result from the relatively small number of samples collected from each plot.

As such a dense sampling scale ($0.5 \times 0.5\text{m}$) was required to determine spatial dependence soil Pb and Zn variation at the Nuns Moor site was considered as occurring over such a short distance that it could be treated as purely random (Section 5.3.3). The lack of spatial dependence provides an insight into the manner in which metals are held within the soil highlighting their association with small compartments of the soil. A high degree of concentration variation identified during quality control

checks of sub samples also accentuates this point (Appendix 3). The lack of spatial structure indicates that a limited number of samples may be used to assess the mean value of the metals at this site. This may be achieved with any spatial distribution of sampling sites (Woperies *et al.*, 1988).

Sampling on such a fine scale ($0.5 \times 0.5\text{m}$) is both, time consuming and expensive and therefore not realistic over a large area. A nested sampling technique may therefore be employed to determine the approximate scale of variation using as few samples as possible to inform a second stage of sampling whereby variograms may be estimated more accurately and over a suitable range (Oliver and Webster, 1991). Such a technique would have provided an insight into the spatial dependence of Pb and Zn at the Nuns Moor site, preventing wasted resources on sampling at both too coarse and too fine a scale. Sampling at a scale greater than the range of spatial dependence produces a flat variogram with no spatial structure, whereas sampling at a scale far less than the range is an unnecessary waste of resources.

Geostatistical techniques, namely kriging, are used to produce surface interpolations, estimating values of a variable at non-sampled locations within a sampled area. The method of kriging takes into account the spatial structure of a variable, determined by its variogram, considering the influence of each sample point location by the assigning weights (Appendix 6). Assuming the variogram has been properly determined and modelled, kriging should produce a reliable surface interpolation. However, nugget variances have been shown to lead to over estimation of the variable at the sample point locations (Webster and Oliver, 1990), a problem that may be avoided, as in this present study, by orientating the prediction grid so that none of the nodes correspond with the sample point locations (Kaluzny *et al.*, 1998).

Kriged interpolations and pixel maps for plot III were noted as producing very similar results, indicating that variograms had been determined with good reliability (Sections 5.2.3.3 and 5.4.1). The kriged interpolations added detail to concentration maps determining the concentration of non sampled areas based on the spatial structure of variation within the plot. Pixel maps on the other hand, used blocks of concentration often indicating dramatic changes from one concentration to another.

The reliability of an interpolation may only be properly tested by comparing the calculated and actual value of the variable from a number of non-sampled locations within the sampled area. Reliability was not tested in the present investigation however, the likelihood of the two corresponding is low, considering the micro-scale nature of spatial variability (Sections 5.2.3.3 and 5.4.1) and within sample heterogeneity identified by this investigation (Appendix 3). Calculation and mapping of estimation variances for the kriged interpolation does, however, enable an assessor to identify locations where variances are higher and sampling must be increased to improve estimates (Oliver and Webster, 1991). Estimates may therefore be determined with a known degree of reliability. The required reliability with which an interpolation is produced, depends upon the relative hazard associated with the contamination, for example, if concentrations are close to threshold or guideline values a higher degree of reliability will be required to determine whether the site should be classed as contaminated.

Disjunctive and indicator kriging are also important techniques for use within soil survey, however, due to time constraints have not been used during this investigation. Disjunctive kriging enables determination of the probability that data does or does not exceed a given threshold, of particular importance in areas where estimates of pollutant concentrations are close to a threshold. Indicator kriging however, utilises separate variograms produced for a series of cut-off (indicator) values to determine the proportion of an area above or below a threshold. These two techniques shall be used in order to further this research.

8.3 FRACTIONATION AND BEHAVIOUR OF Pb AND Zn

It is generally recognised that the behaviour of trace metals in the environment is determined by their specific physicochemical forms rather than by their total metal concentration (Tack and Verloo, 1995) with partitioning known to have a profound influence on environmental mobility and toxicity. The soil is a dynamic environment subject, as the result of both natural processes and anthropogenic activities, to changes in edaphic conditions. Such changes include a complex range of physico-chemical processes that dictate availability and mobility of metals within the soil. During this

investigation Pb and Zn partitioning were determined at one particular time, however, it was recognised that the soil is in a constant state of flux. All forms of trace metals may be released into the soil solution, although do so at different rates under varying soil conditions. In general, some are slow, ie. the release of those metals held within soil minerals, whilst others are rapid, i.e. the release of metals held by the surfaces of soil particles. The degradation of organic matter, for example, will lead to the release of heavy metals held in the oxidisable form. These metals may become available for plant and animal uptake, movement down the soil profile or most likely be held within the soil by another mechanism.

The behaviour, or more importantly the mobility and bioavailability, of Pb and Zn within soil was inferred by examination of metal partitioning within the top and sub soil layers of plot I (Sections 6.2 and 6.3). The BCR method of sequential extraction was used to divide total metals into four fractions, exchangeable, reducible, oxidisable and residual on the basis of ease of extractability (Section 4.3.1 and Appendix 2). Single samples were subjected to extraction by increasingly strong reagents, hence extracting the Pb and Zn fractions held within the soil by increasingly stronger mechanisms. The order of ease of extractability and hence availability is, exchangeable > reducible > oxidisable > residual. As the exchangeable fraction represents the most soluble and mobile portion of total metal a higher percentage of this fraction will indicate greater potential bioavailability and hazard. In addition, ratios of top to sub soil concentrations have been examined (Section 6.5). Lower ratios indicate either a natural geological source of the metals or potential movement down the soil profile, depending on the degree of contamination. Contamination as a result of an anthropogenic source will tend to result in enrichment of metals within the top soil.

The behaviour of heavy metals within soil involves a very complex set of interactions that this project only goes part way to explain having examined selected soil properties only. The project aims to determine qualitatively, the relative hazard¹ associated with

¹ relative hazard – the hazard associated with heavy metal contaminants depends not only on the concentration of the total metal but also on toxicity, with the mobility and hence availability of a metal contaminant depending upon its partitioning within the soil. It is the exchangeable, most readily available fraction that poses the greatest risk although both the reducible and oxidisable fractions of a metal have the potential to become available under certain edaphic conditions (e.g. reducing or oxidising

possible changes in edaphic conditions (pH, organic matter content, CEC), investigating the effects of soil properties on metal partitioning within the top and sub soil layers of plot I. The effects of soil properties have been examined using Pearsons Product Moment Correlation and regression (Section 7.3.3).

8.3.1 Pb and Zn partitioning

The spatial pattern of the Pb fractions was similar to that of the total metal within the top and sub soil, although the four Zn fractions exhibited less clear spatial structure (Sections 5.2, 6.2 and 6.3). Notable differences were seen in the spatial distribution of the Zn fractions that bore little resemblance to the total metal. Spatial distribution was hotspot in nature with single samples exhibiting high concentrations often adjacent to others of low concentration. The hotspot nature of the contamination reflected the association of metals with small components of the soil, often individual particles. Variograms exhibiting large nugget variances also highlighted the lack of spatial structure (Sections 5.3 and 6.4). The lack of correspondence between the spatial distribution of the two metals points to separate sources of the Pb and Zn contamination.

In general, samples exhibiting higher total Pb concentrations exhibited higher concentrations of all four fractions indicating that concentrations of the fractions increased proportionately. Zn fractionation appeared to be more complicated than that of Pb. Ordination in the planes of PC1 and PC2 highlighted, via clustering, the close association and similar partitioning of the Pb fractions within the top and sub soil layers of plot I. Lack of clustering of the Zn fractions, however, confirmed the less consistent partitioning of Zn within the two soil layers (Section 7.3.3).

Sequential extraction identified radical differences in the partitioning of the heavy metals Pb and Zn within the soil of plot I, providing valuable information regarding the mechanisms by which the metals are held within the soil. Pb fractionation was dominated by the reducible and oxidisable forms ($\approx 80\%$) extracted via chemical reduction and oxidation of the soil, respectively (Figure 6.7). The reducible fraction is

conditions). This risk may be associated with human, plant, animal and ecological health, in addition to contamination of water supplies by the movement of the contaminant through the soil profile.

documented as representing those metals specifically adsorbed to the surfaces of Fe and Mn oxides and hydroxides, a mechanism known to be strongly dependent on acidity. The oxidisable fraction is associated with those metals both organically bound and attached to sulphates and hence considered to be strongly related to soil organic matter content. Other studies conducted within urban areas identified a similar proportion of Pb constituting the combined reducible and oxidisable fractions, however, partitioning differed between the two fractions (e.g. Gibson and Farmer, 1986; Chlopecka *et al.*, 1996). Fractionation differences are thought possibly to result from different extraction methodologies (Section 8.3.3).

Mirroring the results of numerous other studies (e.g. Gibson and Farmer, 1986; Ma and Rao, 1997), soil total Zn was dominated by the potentially unavailable residual (60-65%) fraction extractable only by strong and boiling acids (Figure 6.7). The residual fraction represents those metals held within the lattice of silicate minerals that are unlikely to be released even if conditions alter radically. A weak association (identified via Pearsons correlation) between the immobile top and sub soil Pb residual fractions, possible results from the tendency for residual metals to remain firmly held within the lattice of silicate mineral (Yong and Galvez-Cloutier, 1993).

In comparison to Pb, Zn exhibited a higher proportion of the most readily available exchangeable fraction (6-11% versus 8-16%) (Sections 6.2 and 6.3). This fraction represents those metal cations retained by non-specific adsorption to the permanent negative charge sites of silicate clays and pH dependent sites of organic matter and constitutes the most soluble and mobile portion of soil heavy metals. The relative proportion of the exchangeable fraction possibly reflects the status of Zn as an essential trace element required to maintain plant health (Ross, 1994). Pb on the other hand is toxic and exhibits no known essential function. Soil Zn was therefore identified as more readily available than soil Pb, an order of availability that has been documented by numerous other studies (e.g. Merrington and Alloway, 1994; Lee and Touray, 1998). Despite a higher proportion of exchangeable Zn indicating that the Zn is more available than Pb, the relative partitioning of the remaining three fractions of the two metals reflects the greater tendency for Zn to become unavailable once in soils (Ma and Rao, 1997). The proportions of Pb and Zn firmly held within the reducible,

oxidisable and residual fractions severely restricts the potential for downward movement of both elements.

Slight disparities were noted in Pb and Zn fractionation between the top and sub soil layers of plot I, although tests showed these differences were not significant. In comparison with the top soil, the sub soil exhibited almost twice the percentage of the most readily available exchangeable Pb fraction, indicating possible downward movement of Pb within the soil profile (Section 6.2). In contrast to Pb, the top soil contained a higher proportion of exchangeable Zn than the sub soil. Differences in top and sub soil partitioning could also result from corresponding soil property variation and/or different sources of metals within the two soil layers (Section 6.3). On average the top soil exhibited a higher organic matter content, CEC and pH than the sub soil layer. Organic matter is considered to be an effective scavenger of Pb within the surface horizons of polluted soils, severely restricting down profile movement (Fergusson, 1990). A lower organic matter content possibly explains the marginally lower proportion of oxidisable Pb and oxidisable Zn within the sub soil layer in comparison to the top soil layer.

8.3.2 Importance of the exchangeable fraction

The exchangeable fraction constituting the most soluble, mobile and hence bioavailable form of heavy metals within soil is of greatest importance in assessing the potential hazard associated with metal contamination. Studies have used the ratio of total to exchangeable metal concentration as an index of potential mobility of metal within soil (e.g. Mellor and Bevan, 1999), in addition to inferring potential availability of metals for uptake by plants. Relationships between heavy metal fractionation and plant uptake have been well documented (e.g. Dudka *et al.*, 1996; Jung and Thornton, 1996; Logan *et al.*, 1997). The majority of these studies have focused on agricultural crops, particularly foodstuffs, the contamination of which is of potentially higher risk to the human population.

The relationship between Pb in soil and plants has been identified as linear displaying a low gradient indicating that only a small proportion of soil Pb is available for plant uptake (Dudka *et al.*, 1996). In general, plant available heavy metals are extracted with EDTA, the reagent thought to best represent uptake by plants. Time constraints

dictated that such relationships could not be examined directly during this present investigation with equivalent extractions from the soil and grass of plot I not conducted. However, inferences regarding plant uptake can be made from the most readily available exchangeable fraction, a proportion of which is available for uptake. It is recognised that uptake and accumulation of heavy metals, particularly Pb, by the grass at plot I may raise concerns regarding the health of livestock grazed at this site.

Certain soil conditions affect the degree of heavy metal uptake by plants. Larger amounts of Pb are taken up by plant roots under soil conditions of low acidity, CEC and organic matter content, these properties exerting a profound influence on metal form and hence biological availability. Pb binds to organic matter, for example, reducing uptake by the conventional processes of soluble ionic movement. In general, the more soluble a metal the greater the plant uptake. Despite the well documented toxicity of Pb, research has highlighted little affect of Pb on plant health (Jones, 1983; Jinadasa *et al.*, 1997), the real danger lying with Pb that enters the food chain.

Certain plant species have been noted as able to regulate metal uptake at the soil-root interface, clover, for example, tends to contain larger amounts of trace elements than grasses. Moreover, certain accumulator plants take up very large amounts of specific metals experiencing no toxic affects; such plants are utilised as a method of site remediation. Plant trace element contents increase with maturity in addition to being influenced by seasonality. Lower concentrations of Pb have been identified within grass during summer than winter months (Mitchell and Reith, 1966), a factor which has practical implications for the grazing of the Nuns Moor site. Grass Pb concentrations are lowest throughout the summer grazing season, rapid plant growth during the warmer months reducing the amount of time over which grass can accumulate metals. Cattle have been shown to ingest up to 10 times the amount of elements in the form of soil than herbage (Thornton, 1974) hence the soil-animal relationship may override the soil-plant-animal relationship at the Nuns Moor site. In addition soil organisms, such as earthworms, known to accumulate metals when living in contaminated soil may be at risk from high concentrations of soil Pb at this site.

The present investigation, despite determining that a relatively small proportion of total Pb and Zn within the soil of plot I was of the exchangeable form emphasised that

soils exhibiting high total metal concentrations will exhibit high concentrations of the exchangeable fraction (Section 6.2). The study identified exchangeable Pb concentrations in excess of 400mg/kg, concentrations that regardless of the other three fractions exceed the Dutch B value (Appendix 1). Alone, concentrations of the exchangeable fraction would indicate the need for further investigation had the site been located within the Netherlands. Concentrations in excess of 400mg/kg equate to >20% of the allowable levels of Pb within the soil of parks, playing fields and public access land under the British ICRL guidelines. Despite the relative importance of the exchangeable fraction, in general, legislative guidelines regarding heavy metal contaminated land have yet to specify maximum allowable levels of this fraction (Section 8.4.2).

Significant correlations between the exchangeable Pb fraction within the top and sub soil suggest possible movement down the soil profile, raising concerns regarding the potential contamination of groundwater. A higher proportion of exchangeable Pb within the sub soil provides further supports these concerns. Fractionation differences may however be related to differences in soil properties within the two soil layers.

8.3.3 Implications of extraction methodology

Numerous chemical fractionation methods have been developed and applied over the past two decades in an attempt to understand the behaviour of heavy metals within soil, sediment and water. Despite 20 years of research into sequential extraction schemes (Quevauviller *et al.*, 1997) the chemical fractionation of metals is still in the early stages, with the majority of papers concentrating on method development. A number of problems have been identified with such schemes related mainly to non-selectivity of reagents, redistribution effects (Tack and Verloo, 1995) and extraction efficiency (Harrison, 1987). As a result of these uncertainties the results from sequential extraction procedures are defined according to the reagents used.

The need for consistency has led to a growing body of research into the BCR extraction scheme (used during this study), which highlighted a number of stages where inconsistencies may arise. In general, the pH in step two has been identified as the most critical, affecting the amount of metal extracted (Davidson *et al.*, 1999; Sahuquillo *et al.*, 1999). Despite this, sequential extraction procedures are useful

within the field of environmental geochemistry, providing an indication of the reactivity and potential mobility of the metals within soils. Results must however, be interpreted with care and in the context of other observations (Tack and Verloo, 1995). Despite significant correlations being identified between metals extracted at different stages of the BCR technique and the corresponding steps of Tessiers' scheme (Zhang *et al.*, 1998) notable differences in partitioning have also been identified. The distinct partitioning patterns of Pb and Zn within the top and sub soil of the Nuns Moor site confirm that sequential extraction is of value in establishing the partitioning of heavy metals within urban soils (Sections 6.2 and 6.3).

Concentrations of top soil exchangeable Pb identified by this present study were comparable to those identified by Mellor and Bevan (1999) when examining a similar area of Nuns Moor. However, the proportion of exchangeable to total Pb identified by the present study was notably lower. Differences in the proportion of exchangeable Pb are thought to be related to extraction methodology as Mellor and Bevan (1999) extracted what they defined as 'plant available' Pb using more concentrated acetic acid. Similar studies have also identified different proportions of the other Pb and Zn fractions. Again, these differences are thought to reflect different extraction methodology; a number of schemes use different strength reagents extracting the reducible fraction in two stages. Gibson and Farmer (1986), for example, identified 70-75% of total lead within the soils of Glasgow as being reducible and oxidisable, a similar proportion to the present study. However, in contrast to the present study the authors determined that the reducible fraction was dominant, exhibiting a far higher proportion than the oxidisable fraction. As a smaller proportion of the total Pb was extracted as reducible by the present study, a larger proportion was available to be extracted by the next reagent and hence included within the oxidisable fraction. However, differences in both contaminant source and soil properties are known to play a vital role in metal partitioning.

8.3.4 Sources and partitioning of heavy metal contamination

The partitioning of metals within the soil partially reflects the source of the contaminant, with metals of anthropogenic and geological origin thought to exhibit different mobilities and availabilities. Research has however, as highlighted by the present study, produced contrasting theories regarding the relative partitioning of

metals resulting from these sources. Ratios of top to sub soil metal concentrations may also be used to indicate sources of contamination with evidence of top soil enrichment pointing to an anthropogenic source.

When examining a similar geographical area to the present study Mellor and Bevan (1999) determined that higher proportions of the more mobile, 'plant available' fraction of Pb were found within the soil of rural areas of the Ouseburn catchment in addition to the Town and Nuns Moors. The authors concluded that more soluble, mobile forms were derived from weathering and pedological alteration of underlying parent materials. In contrast, the less mobile, more persistent forms of Pb, found within the more urban parts of the catchment were associated with industrial and urban activity. The present study has however identified exceptionally high concentrations of total and hence exchangeable Pb within the soil of Nuns Moor that far exceed those likely to accumulate as a result of natural weathering (Section 6.2). The high soil total Pb concentrations point therefore to an anthropogenic source of Pb contamination, although no industrial activity can be directly associated with the Nuns Moor site (Section 3.3.1). The result is more in line with that of Chlopecka *et al.* (1996) who conversely suggest that metals from anthropogenic sources are more mobile than those derived from parent material. In addition, the relatively small size of the contaminated plot and patchy nature of the metal distribution, further indicate an anthropogenic source, most likely of aerial descent.

Heavy metal enrichment of top soil in comparison to sub soil has been identified at Nuns Moor site (Section 6.5) providing evidence of possible aerial deposition of anthropogenic contaminants at the site. In general, heavy metals will accumulate at the soil surface, usually within the top few centimetres, with concentrations diminishing with depth. Metals will tend not to leach down the soil profile being held by adsorption onto the surfaces of clay minerals and organic matter. In comparison to the sub soil, plot I top soil Pb and Zn concentrations were enriched by on average 210% and 30%, respectively. Total Pb concentrations were also notably higher than total Zn, that fell well below background concentration for the area (calculated by Aspinall *et al.*, 1988, Appendix 1). Associations, although weak, between the Pb fractions within the top and sub soil layers of plot I suggest a similar source of Pb within the two soil layers.

The aerial deposition of fertilisers and pesticides used for the maintenance of golf courses and minor fuel spillage as a result of trail bike use have been identified as two possible sources of Pb contamination at the Nuns Moor site (Section 8.2.3). However, research into Pb fractionation within soils contaminated as a result of agrochemical impurities (Taylor *et al.*, 1995) and petrol derived Pb (Harrison *et al.*, 1981) has shown the exchangeable fraction to be low, less than or equal to 1%; considerably less than the present study. Fractionation differences may result from differing soil conditions, eg. pH or quantity and type of organic matter (Section 8.3.5), or the relative selectivity of different extractants used during different sequential extraction schemes. In general, percentages of exchangeable Pb have been determined as low at less than 5% (Fergusson, 1990).

Despite slight top soil Zn enrichment, the majority of Zn within the soil of plot I was thought to be of geological origin. As metals from geological sources tend to exhibit lower mobility and higher persistence than those derived from anthropogenic sources this may explain the relative immobility of Zn (high proportion of the residual metal) within the soil. However, slight accumulation of Zn at the soil surface was thought to result from either an anthropogenic input or natural biological cycling of the metal through the grass. A higher percentage of residual Zn within the sub soil in comparison to the top soil again indicated the possibility of different sources of Zn within the two soil layers. Alternatively partitioning differences could be a consequence of differing edaphic conditions within the two soil layers.

Within the top soil, corresponding Pb and Zn fractions exhibited no significant correlations, although some were noted within the sub soil. The lack of associations between the corresponding Pb and Zn fractions confirmed the different patterns of metal partitioning identified in Section 7.3.3.3, suggesting that the two metals may have originated from different sources. Differences in partitioning were also thought to reflect the different edaphic influences on the two metals. The failure of a non-hierarchical clustering technique to determine a single optimum classification when all variables were included within the analysis further suggests not only a lack of spatial structure but also a lack of association between the two metals. Again, indicating that the two metals are likely to have originated from different sources.

From the evidence presented above it appears that the determination of heavy metal fractionation alone is insufficient to enable conclusions to be drawn regarding the source of heavy metals contaminants within soil. Edaphic conditions are known to play a vital role in heavy metal partitioning often dictating the complex array of physico-chemical interactions occurring within the soil environment. Research has shown soils contaminated by the same source to display notably different heavy metal fractionation (Ma and Rao, 1997). Further information, regarding the source of Pb contaminants can be gained by examination of isotope ratios. Pb from different sources, for example, geological and petrol derived exhibit different ratios of Pb, 206, 207 and 208 (e.g. Walraven *et al.*, 1997). An investigation of this kind would confirm or disprove the possible sources of heavy metal contamination at plot I suggested above.

8.3.5 Influence of soil properties on Pb and Zn mobility and availability

The roles of pH (e.g. Chuan *et al.*, 1996; Sauve *et al.*, 1997; Hooda and Alloway, 1998), organic matter (e.g. Hargitai, 1995; Sauve *et al.*, 1997; Mellor and Bevan, 1999) and CEC (e.g. Chlopecka *et al.*, 1996; Abu-Rukah, 1998; Hooda and Alloway, 1998) in controlling the behaviour and mobility of the metals Pb and Zn in soils are well documented. Although, these properties have not always been identified as exerting a direct effect on heavy metal fractionation. The influence of these three soil properties on both total metal concentration and metal partitioning was examined within the soil of plot I, variable pH, organic matter content and CEC within the plot making such investigations possible. Associations were examined using Pearson's correlation, regression and PCA. Numerous significant correlations were identified, however the majority were classified as weak exhibiting correlation coefficients $<|0.45|$. Regression analysis determined that levels of explanation were often low. For the purposes of this investigation, only the most significant associations have been interpreted, as not only do they help explain the behaviour of Pb and Zn, but exert the greatest effect on the potential hazard of the metals.

pH

Despite pH being considered the most important factor affecting heavy metal solubility and mobility within the soil (e.g. Chuan *et al.*, 1996; Rieuwerts *et al.*, 1998) few statistically significant correlations ($p < 0.05$) were noted between pH and the total and

metal fractions within the soil of plot I (Section 7.3.3.1). Most notably pH was only significantly associated with the top soil residual Pb fraction, exhibiting a weak negative association. Hence, concentrations of the most strongly held residual fraction, increased with decreasing pH or increasing soil acidity, reducing metal solubility and increasing soil metal retention. This result contradicts that identified by many other studies. On the whole pH has been noted as exerting the greatest effect on the bioavailable (extractable) metals (Rieuwerts *et al.*, 1998) being positively correlated with metal retention (Hooda and Alloway, 1998).

In contrast to the top soil, sub soil total Pb and three of the Pb fractions (exchangeable, reducible and oxidisable) displayed significant, although weak, negative associations with pH (Section 7.3.3.1). Hence, Pb concentrations, with the exception of the least available residual fraction, increased with increasing acidity. The greatest correlation coefficient was noted with the exchangeable fraction, solubility, mobility and availability of Pb increasing with decreasing pH. Similar pH ranges were determined within the two soil layers, although on average, the sub soil was marginally more acidic. It is thought unlikely that this subtle difference in pH would affect Pb availability. More significant differences in other soil properties, for example organic matter, may be of greater importance.

In general, the exchangeable fraction represents those metal cations retained by non-specific adsorption to the permanent negative charge sites of silicate clays and the pH dependent sites of organic matter (Ross, 1994). It is thought therefore that, as the top soil contained approximately twice as much organic matter as the sub soil, the pH dependent sites of organic matter will be of greater importance for the binding of Pb cations within the top soil. Clay is considered to be of greater importance within the sub soil layer. However, the lack of association between pH and exchangeable Pb within the top soil, in addition to, the existence of such a relationship within the sub soil indicates that organic matter may be more important for the adsorption of Pb cations within the sub soil layer. Type rather than amount of organic matter may therefore be of greater importance for the binding of Pb cations.

In comparison to Pb, soil pH exhibited far fewer associations with the Zn fractions displaying just one significant, yet weak association with sub soil total Zn (Section

7.3.3.2). This association was positive indicating an increase in total Zn concentration, i.e. Zn retention, as soil pH increased. The higher sub soil total Zn concentration within less acidic soils may be explained in terms of metal retention. Higher concentrations of residual Zn under such pH conditions determine that the more mobile fractions exhibit lower concentrations. Consequently, less Zn is available for uptake by plants or movement down the soil profile and hence Zn retention increased. pH has been suggested as the most important parameter influencing soil Zn reaction, with solubility of Zn decreasing with increasing soil pH (Kiekens, 1995). However, significant associations were not identified between pH and the most readily available fraction suggesting that the pH range within this study may be too narrow to identify a significant relationship. Harter (1983), for example, determined that the effect of pH on Zn fractionation was most dramatic above pH 7.0 – 7.5, outside the range of this present study.

Organic matter

Organic matter has been identified as a strong retention mechanism for metal within soil, severely restricting movement down the soil profile (Ferguson, 1990). Despite this, a number of studies have failed to draw definite conclusions regarding the role of organic matter and metal partitioning (e.g. Sauve *et al.*, 1997). This present study however, identified, via Pearsons Correlation, numerous associations between organic matter and concentrations of total and fractions of Pb and Zn within the two soil layers (Sections 7.3.3.1 and 7.3.3.2). Organic matter is considered to be, of those studied, the most important soil property influencing soil Pb and Zn partitioning, mobility and availability within the soil of plot I.

The majority of associations between organic matter and Pb within the soil of plot I were identified as weak, displaying correlation coefficients of $<|0.45|$. Within both soil layers the strongest associations were exhibited with the oxidisable fraction and total metal concentration (Sections 7.3.3.1). Associations identified within the sub soil displayed higher correlation coefficients than those within the top soil. In general, organic matter was most strongly associated with the oxidisable Pb fraction, higher concentrations being found within samples containing higher percentages of organic matter. The oxidisable fraction represents those metals bound to organic matter by organic complexation in addition to that associated with sulphates, explaining the

association between the Pb fraction and organic matter. A significant proportion of total Pb is of the oxidisable form further explaining the association between total Pb and organic matter.

Despite the sub soil layer containing, on average, half the organic matter of the top soil, organic matter was noted as exhibiting a greater influence on oxidisable Pb within the sub soil. Type of organic matter may therefore be of greater importance than amount for the binding of heavy metals (Hargitai, 1995; Mellor and Bevan, 1999). Metal retention has been associated with both the insoluble humic and soluble fulvic acids constituting organic matter, however, Pb despite being generally organophilic is most strongly associated with the humic component (Hargitai, 1995). The sub soil is known to contain a higher proportion of the humic fraction than the top soil (Rowell, 1994) resulting in the stronger association between sub soil organic matter and oxidisable Pb concentration.

The top soil exchangeable Zn fraction exhibited a positive moderate association with organic matter within plot I, thought to reflect the role of organic matter as a site for the binding of metal cations (Section 7.3.3.2). Organic matter provides pH dependent sites for the non-specific electro-static adsorption of metal cations, hence top soils containing a higher proportion of organic matter will provide more exchange sites than either top or sub soils of lower organic matter content. The strength of the electrostatic association is dependent on both valency and hydrolysis of heavy metal cations (Ross, 1994), with those of higher valency and/or hydration exhibiting a preference for adsorption onto exchange sites (Harter, 1983). It was noted that organic matter content was less strongly associated with exchangeable Pb, than with exchangeable Zn, possibly reflecting the higher degree of hydration of Zn cations. The different degrees of hydration of Pb and Zn may also explain the higher proportion of total Zn within the exchangeable form. Investigations into Zn adsorption have shown both clays and organic matter to adsorb Zn quite strongly (Kiekens, 1995) with the type of sub soil organic matter possibly explaining the lack of statistically significant association between sub soil organic matter content and exchangeable Zn. Within the sub soil, it is possible that clay minerals play a more important role in providing exchange sites for the binding of Zn. Under acid conditions Zn has been identified as adsorbing to cation exchange sites rather than being chemisorbed and highly affected by organic

ligands as under alkaline conditions (Kiekens, 1995); this possibly explains the moderate association between exchangeable Zn and organic matter identified by the present study.

Within plot I, an increase in soil organic matter content has been seen to exert different influences on the mobility and availability of Pb and Zn. Increases in the soil property have been shown to increase Pb retention within the soil through increased concentrations of the relatively immobilisable oxidisable Pb fraction. Conversely, Zn availability has been increased, as a higher organic matter content was shown to result in higher concentrations of the most readily available exchangeable fraction. Organic matter is thought therefore to provide an important site for the non-specific adsorption of cations, with Zn being adsorbed in preference to Pb due to its higher degree of hydration.

CEC

Within the top soil, CEC exhibited a statistically significant, yet weak, positive relationship with only the oxidisable Pb fraction (Section 7.3.3.1). This fraction was also strongly associated with soil organic matter, reflecting the relationship between soil organic matter content and CEC. Within the sub soil however, CEC was associated with total, in addition to three Pb fractions (reducible, oxidisable and residual). All four relationships were positive but weak. Despite the sub soil exhibiting a notably lower CEC than the top soil, CEC was seen to exhibit a greater influence on the sub soil Pb fractions than the top soil Pb fractions. This difference is thought to result from the sub soil containing a higher proportion of clay, clay minerals and the organic matter type important for providing exchange sites for cations. A number of studies have investigated the influence of CEC on Pb concentration (e.g. Abu-Rukah, 1998; Hooda and Alloway, 1998). Some determined that CEC did not influence the relative proportions of heavy metal forms in any consistent manner (e.g. Chlopecka *et al.*, 1996). Fractionation differences were thought to reflect different soil types examined during the above investigations. In general, Harter (1983) determined that soils exhibiting the highest CECs exhibited the highest heavy metal sorption. This relationship was not quantified.

CEC exhibited statistically significant associations with all top soil Zn variables except the residual fraction (Section 7.3.3.2). All four associations were positive but weak. In contrast to the Pb fractions the association between CEC and exchangeable Zn displayed the highest correlation coefficient. CEC is a measure of the ability of soil to attract and hold cations, these being held by both non-specific and specific adsorption. The higher proportion of exchangeable Zn in relation to exchangeable Pb possibly reflects preferential adsorption of Zn versus Pb cations due to higher Zn hydration.

Throughout the present study, CEC was generally found to explain the least variation (determined via regression analysis R^2 values) within the Pb and Zn fractionation of the three soil properties examined, indicating that the property is of least value when attempting to determine both Pb and Zn fractionation. Increases in CEC, despite exerting differing influences on the two metals have been shown to increase concentrations of Pb and Zn within the potentially available fractions. The ratio of exchangeable metal to CEC has been identified as a good indicator of a soils immobilisational capacity for heavy metals (Gupta *et al.*, 1996). In this investigation, the ratio was found to be very erratic, suggesting that soil immobilisational capacity is highly variable.

8.3.6 Soil property changes: possible implications

Relationships identified between soil properties, total metal concentrations and metal fractionation highlight possible implications of changing edaphic conditions within the soil of plot I. Certain soil properties have been identified as influencing the solubility, mobility, and availability of Pb and Zn within the soil. The most readily available exchangeable fraction is of greatest importance when attempting to assess the hazard associated with soil heavy metal contamination. Links have been associated between the concentration of exchangeable metals within soil and plants in addition to the exchangeable fraction being considered the most readily available to mammals and soil organisms.

Despite an increase in soil pH being identified as decreasing concentrations of the residual Pb fraction within the top soil of plot I, techniques such as liming have been used for a number of years to reduce heavy metal solubility within the soil. Liming, neutralises acidity reducing the solubility of metals, such as Pb within the soil. In

general, research has determined that Pb is more mobile at low pH values (Chuan *et al.*, 1996)). The main objective of this remediation technique is to decrease metal availability to the food chain rather than remove metals from the soil. At the other end of the scale, acid rain has the potential to increase soil acidity and hence metal solubility. The natural degradation of organic matter also increases the acidity of soil.

The oxidisable fraction, representing those metals both organically bound to organic matter and associated with sulphates, has been identified as one of the dominant fractions of Pb within the top and sub soil of plot I. The natural degradation of organic matter will therefore, in addition to increasing soil acidity result in the slow release of metals held in the oxidisable fraction. In addition organic matter provides non-specific sites for the electro-static adsorption of heavy metals. Metals released as a result of organic matter degradation will become available for plant uptake, down profile movement or most likely uptake by another binding mechanism. Degradation of organic matter is a natural cycling of metals within the soil.

Certain areas of the Nuns Moor site have been noted as experiencing water logging during wet winter conditions, with small puddles of water standing on the surface. Under waterlogged conditions soil pores are often completely filled with water, substantially reducing the volume of air and therefore oxygen within the soil. Reduction in soil oxygen levels leads to increased activity of anaerobic bacteria and the formation of reducing conditions. Reducing conditions have been shown, by the sequential extraction technique used during this study, to release metals specifically adsorbed to the surface of Fe and Mn oxides and hydroxides. This fraction, along with the oxidisable, has been identified as a dominant mechanism for Pb retention in the top and sub soil layers of plot I. On release this metal will most likely become available for retention by another mechanism. Hence, water logging at the Nuns Moor site has potential implications for soil metal retention.

8.4 RELATIVE SEVERITY OF HEAVY METAL (Pb AND Zn) CONTAMINATION

Attempts to determine the relative severity of soil heavy metal contamination have been complicated by the dramatic variation of threshold values currently in use within Europe (Appendix 1). Such thresholds, stating a total metal concentration above which soil is considered to be contaminated, indicate that soil multifunctionality might be adversely affected, and signal the extent of contaminant accumulation (Gupta *et al.*, 1996). In general, the Dutch have imposed the most stringent guidelines that state not only optimum concentrations for various contaminants within soil but also action thresholds, above which sites must be remediated. The Dutch have adopted what has become known as the multifunctionality approach, whereby all land must be remediated to a standard suitable for any use (Section 2.7). The UK, however, only specifies 'trigger' concentrations above which some form of site assessment is necessary. Trigger concentrations within the UK vary according to planned land usage with lower values set for domestic gardens and allotments than for parks, playing fields and public open spaces (Section 2.7). Aspinall *et al.* (1988) determined highest probable thresholds for uncontaminated soils in Tyneside (HPTULT) using a graphical approach defined by Davies *et al.*, (1983).

8.4.1 Extent and severity of contamination

Aspinall *et al.*, (1988) defined the uncontaminated threshold for Tyneside soils to be 80mg/kg for total Pb and 345mg/kg for total Zn, under which scheme the majority of samples collected during this present investigation are classed as contaminated with respect to Pb (Section 5.2). All samples collected from the Town Moor, Nuns Moor and S. Gosforth sites exceed the Pb threshold, together with 62% of the samples collected from the Hazelrigg nature reserve. All samples collected from plots I, II and III also exceeded the HPTULT value specified Aspinall *et al.* (1988). These sites therefore contained higher than background concentrations of Pb. Only one sample collected from each of the Town Moor, Hazelrigg and S. Gosforth sites exceeded the threshold for Zn, with no samples collected from Nuns Moor, including the three plot sites, exceeding the HPTULT value.

The comprehensive 'New Dutch List', updated from the Dutch ABC list specifies action thresholds as 530mg/kg and 720mg/kg for soil Pb and Zn, respectively. If used as a reference point in the present investigation, such regulations categorise approximately 20% of the Town Moor samples, 33% of the Nuns Moor samples and 3% of the S. Gosforth samples as being contaminated with Pb. Approximately 70% of top soil and 40% of sub soil samples collected from plot I also exceeded this Dutch action threshold, in addition to 80% of plot II and plot III samples. Only one sample from the Hazelrigg nature reserve and one from S. Gosforth exceeded the action threshold for Zn. In contrast, only three samples, collected from the four sites exceeded the less stringent British ICRCL trigger concentration, 2000mg/kg, for soil Pb in parks playing fields and public open spaces. However, 25% of top soil and 3% of sub soil samples collected from plot I exceeded the British trigger threshold, in addition to 30% of plot II and 25% of plot III samples. No corresponding threshold exists for Zn within this scheme.

Under the different legislative systems, the four sites and three plots examined during this current investigation exhibited very different levels of contamination. It was noted that a sample classified as being highly contaminated by the Dutch scheme may be classified as uncontaminated by the British ICRCL scheme, regardless of being classified by Aspinall *et al.* (1988) as containing higher than background levels of metal contamination.

8.4.2 Future prospects for metal contamination legislation

Since the adverse health effects of contaminated land were realised, an extensive amount of contamination has come to light. Contaminated land has been identified as a large-scale problem for which the economic cost of clean up is enormous (Willis and Jones, 1996). The UK has been late in its development of a contaminated land policy, which has led, however, to the evolution of what has been seen by some, as a more mature policy. More mature policies have been defined as exhibiting the following characteristics (Willis and Jones, 1996):

- reduced use of unnecessary regulation;
- flexibility in relation to clean-up standards;
- use of economic incentives;

- use of risk assessment techniques in a site specific manner;
- emphasis on re-development of derelict and contaminated land hence reducing pressure on greenfield sites.

The UK policy aims to encourage sustainable development by the re-development of brownfield over greenfield sites. However, others argue that the health risks associated with contaminated land must be minimised by the setting of low trigger thresholds regardless of the economic cost of clean-up (Mellor, in prep.). Scientific uncertainty still remains, but as the impacts of heavy metal contamination on human health become increasingly realised, it seems likely that increasingly stringent trends in environmental legislation will emerge (Mellor and Bevan, 1999). UK trigger thresholds are likely therefore to converge more towards those of the Dutch, with the implementation of a more stringent scheme determining that numerous sites classed under the current British ICRL guidelines as uncontaminated may in the future become classified as contaminated and require remediation.

The future persistence and hazard of heavy metals within the soil may be predicted in view of their partitioning, which could have severe long and short-term environmental implications. Within plot I, soil Pb has been shown to be less mobile and available than soil Zn, exhibiting a lower proportion of the exchangeable fraction (Section 8.3.2). However, notably higher concentrations and toxicity of soil Pb determines that the metal is of potentially greater hazard than Zn. The soil properties, pH, organic matter content and CEC, did not consistently influence the fractionation of the two metals, indicating that changes in edaphic conditions will result in differing degrees of hazard being associated with the metals Pb and Zn (Section 8.4.3). An increase in soil acidity has been shown to increase both Pb and Zn mobility and availability and hence the hazard associated with these metals. An increase in soil organic matter content increased the concentration of the relatively immobile oxidisable Pb fraction and the readily available exchangeable Zn fraction, reducing the hazard associated with Pb but possibly increasing that associated with Zn. An increase in CEC, a property strongly correlated with soil organic matter content, was seen to increase the concentrations of oxidisable Pb.

Despite the knowledge that contaminant availability and mobility are dependent upon form within the soil, the majority of European countries have yet to specify guidelines for the various metallic forms. Two exceptions to this are Switzerland and the German State of Baden-Württemberg, that specify thresholds for both total and mobile / bioavailable forms. Guidelines are exceeded if either one or both of these values are exceeded (Gupta *et al.*, 1996). If legislation is to evaluate fully the adverse effects of metals on human and animal health and the environment, environmental standards must progress in this manner.

8.4.3 The new framework

Following the enforcement in England and Wales of Part IIA of the EPA (1995) in April this year contaminated land has been redefined. Part IIA aims to incorporate the significance of contaminants, determining whether they are causing harm rather than being purely present at a site. The act includes a model based on the Contaminated Land Exposure Assessment Model (CLEA). The model includes three key factors which must all be in place if a contaminant is to cause harm. These factors are (1) a hazard (2) a pathway (3) a target. At the Nuns Moor site, for example, the hazard may be Pb within the soil, the pathway plants or soil dust and the targets cows or humans, respectively.

If the hazard-pathway-target model is to be effective it is essential that contaminants are defined according to their solubility, mobility and bioavailability. The model further highlights the need for contaminant guidelines to be extended to include the partitioning of contaminants at a site. Guidelines must include, at the very least, maximum allowable levels for the bioavailable, exchangeable metal fraction. Guidelines must be set on the basis of scientific research and related to potential toxicity rather than subjective judgement, as is often the case at present. In addition, it is necessary that uptake by plants, for example, or concentrations of bioavailable metals in dust are examined. Risk assessments must be site specific defining the hazard associated with individual sites on the basis of both present and intended landuse. The potential for contaminants to migrate and/or become bioavailable must be examined in relation to possible changes, for example, pH and redox conditions, at a site. In addition, potential risk must be balanced against cost of remediation, although, not at a risk to human or animal safety.

8.4.4 Remediation

Numerous techniques exist for remediation of contaminated land. In general, there are two categories, (1) containment of the contaminant(s), e.g. encapsulation and capping, and (2) removal of the contaminant(s) via biological, chemical or physical methods. Different techniques are more appropriate for use at different sites, depending upon the type, concentration and nature of contaminants present. Remediation methods work by removal of one of the key factors within the hazard-pathway-target model, in general the hazard (source of the contaminant) or the pathway. Remediation of metal contaminated sites requires a certain amount of expertise due to the presence of different concentrations and forms of the metals. In addition, changes in edaphic conditions can alter the fractionation of metals within the soil.

Soil samples collected from plot I, Nuns Moor, were found in approximately 25% of cases to contain quantities of total Pb in excess of the ICRCL guideline, raising concerns regarding the use of the area as open public access land. The area is frequently used by children, with areas of bare soil often exposed during the summer months. In addition, concentrations of exchangeable Pb, the most bioavailable fraction, were found to be high in those samples exhibiting high total Pb concentrations. Concentrations of the exchangeable fraction have been correlated with concentrations within plants, raising concerns regarding the health of cows grazed at the site. Grazing animals are also known to ingest significant quantities of soil. Investigations into grass Pb concentrations would allow this risk to be further quantified. In relation to the whole Nuns Moor site the contaminated area is relatively small, however, it lies close to both housing and a school. Given the high Pb concentrations it seems appropriate that at least part of this site should be remediated in order to reduce potential risk to both human and animal health.

CHAPTER 9

CONCLUSIONS

Summary

This chapter concludes the thesis, reiterating the main findings of the investigation, and re-visiting the original aims of the study. In addition it considers the limitations of the investigation and explores possible avenues for future research. The chapter has been divided into 9 sections. Section 9.1, the introduction, sets the investigation in context, highlighting the novelty of the study. Section 9.2, draws conclusions regarding the complexity of soil Pb and Zn contamination masked by coarse scale sampling. Section 9.3 notes the level of Pb and Zn spatial dependence at a variety of sampling scales, indicating the usefulness of geostatistical techniques. Sections 9.4 and 9.5 draw conclusions regarding the availability and mobility of Pb and Zn, as determined by metal partitioning and examination of relationships between the metal fractions and key soil properties. Section 9.6 summarises the possible sources of the metals within the study sites whilst Section 9.7 draws conclusions regarding relative severity of the metals and possible future changes to environmental legislation. Section 9.8 makes recommendations to managers investigating polluted sites. Finally Section 9.9 highlights the limitations of the study, suggesting some possible future avenues for work within this field.

9.1 INTRODUCTION

The relatively limited number of studies investigating spatial variation of soil heavy metal pollution, particularly within the urban environment, make this investigation useful for those involved in the assessment and development of contaminated land. This study has highlighted some of the problems encountered when attempting to determine the spatial distribution and extent of soil Pb and Zn pollution, in addition to the hazard associated with such contaminants. The investigation has explored the importance of fractionation on the availability of soil heavy metals, in addition to the affects of selected key soil properties on mobility. The study highlights the need for environmental legislation to consider both metal partitioning and changing edaphic conditions in its assessment of hazard.

9.2 COMPLEXITY OF SOIL Pb AND Zn CONTAMINATION

Soil Pb and Zn concentrations have been identified as exhibiting characteristic positively skewed frequency distributions, with elevated concentrations found to occur in hotspot locations. The patchy distribution of Pb and Zn contamination is thought to result from the inherent stability of heavy metals within soil, movement being slow and pathways short. Plot scale sampling at increasingly fine scales ($25 \times 25\text{m}$, $5 \times 5\text{m}$, $0.5 \times 0.5\text{m}$) determined that both concentration and spatial variation of Pb and Zn were at least as great at the finest sampling scale as at the coarsest sampling scale. The results highlighted how sampling density can affect conclusions drawn, confirming that coarse scale sampling can fail to identify the true nature of heavy metal contamination.

9.3 SPATIAL DEPENDENCE AND USEFULNESS OF GEOSTATISTICAL TECHNIQUES

Spatial variability of Pb and Zn concentrations within soil of plots I and II exhibited little spatial structure at the $25 \times 25\text{m}$ and $5 \times 5\text{m}$ scales with the variograms exhibiting large nugget variances, indicative of either micro-scale variation or a lack of spatial continuity. However, a dense sampling network ($0.5 \times 0.5\text{m}$) produced better behaved omni-directional variograms with smaller nugget variances. Zn concentrations within plot III exhibited a bounded type variogram. However, variation occurred over such a short distance that it could possibly be treated as purely random. In this case, mean metal concentrations may be determined by a limited number of samples collected with any spatial distribution.

The surface interpolation produced for total Zn concentrations using the method of punctual kriging gave very similar results to the pixel maps, raising questions regarding the use of complex statistical techniques for this type of investigation. However, geostatistical techniques enable the assessor to determine contaminant concentrations with a known degree of reliability, and are of particular use if concentrations are close to legislative guideline or threshold values. Other types of kriging, namely disjunctive

and indicator can also be invaluable in site investigation, although these methods were not been used during this investigation.

9.4 MOBILITY AND AVAILABILITY OF Pb AND Zn

Sequential extraction determined that the two metals exhibited different fractionation characteristics, although similarities were noted within the top and sub soil layers of plot I. Approximately 70% of total Pb was of the reducible and oxidisable forms, whereas the residual fraction was dominant for Zn, comprising about 60% of the total metal. Zn exhibited a higher degree of mobility and availability than Pb, the top and sub soil exchangeable fractions comprising 12 and 17% and 6 and 11% of the total metals, respectively. However, as soil Pb concentrations were substantially higher than soil Zn concentrations, Pb was considered to be of greater potential hazard. In general, Pb exhibited higher top : sub soil enrichment ratios than Zn, the top soil containing 210% more Pb and 30% more Zn than the sub soil. A Higher proportion of sub soil than top soil exchangeable Pb indicated possible movement of the metal down the soil profile. Top soil enrichment indicated that Pb within the soil of plot I was of anthropogenic origin.

9.5 BEHAVIOUR OF Pb AND Zn

The soil properties, pH, organic matter content and CEC, did not influence the partitioning of the two metals in a consistent manner. Organic matter acted as an efficient scavenger for Pb, exhibiting the most significant correlation with the oxidisable fraction, whilst providing more pH dependent sites for the non-specific adsorption of the exchangeable Zn fraction. CEC, exhibiting a strong association with organic matter content, displayed a positive correlation with the oxidisable Pb fraction. The property exhibited the strongest influence on the sub soil Pb fractions, possibly due to the higher proportion of clay and clay minerals within the sub soil layer. PCA was used to investigate the effects of soil properties on metal fractionation however, despite similarities being identified between the partitioning of top and sub soil Pb within plot I, no soil properties were found to be significantly correlated with the principal

components. Non-hierarchical clustering failed to identify a single optimum classification when all 26 variables were included within the analysis. This highlights both the lack of spatial structure of Pb and Zn variables, in addition to the lack of association between the two metals.

9.6 SOURCES OF Pb AND Zn CONTAMINATION

A number of different sources of Pb and Zn contamination were identified at the four sites. Zn was thought to be mainly of natural, geochemical origin, derived from the weathering of parent materials, whereas elevated concentrations of Pb were thought to result from anthropogenic sources. Possible sources of Pb contamination at the sites included vehicular emissions and fuel spills (Town Moor), contaminants within agrochemicals (Nuns Moor), variations in top soil thickness at restored colliery spoil tips (Hazelrigg nature reserve) and a household lead-acid battery placed on a fire (S. Gosforth). Little evidence exists for identifying the sources of hotspot contamination at these sites, although aerial photographs, and knowledge of past and present landuse have been used to draw inferences.

9.7 RELATIVE SEVERITY OF AND HAZARD ASSOCIATED WITH Pb AND Zn CONTAMINATION

The relative severity of Pb and Zn contamination at the four sites varies according to the system of trigger threshold adopted. Using the least stringent UK ICRCL guideline for Pb within the soil of public access and amenity areas, very few samples collected from the four sites are classed as contaminated. However, approximately 25% of those collected from plots I, II and III exceed this threshold. No equivalent threshold exists for Zn under the UK system. Adopting the more stringent Dutch system of action guidelines, 20% of Town Moor samples, 50% of Nuns Moor samples and one sample from the S. Gosforth site are classed as contaminated. In addition, between 70 and 80% of top soil samples collected from the three plots are also classed as contaminated. Using the statistically derived HPTULT value calculated by Aspinall *et al.* (1988) all samples collected from the Town Moor, Nuns Moor and Gosforth sites are classed as

containing higher than background concentrations of Pb, in addition to 62% of the samples collected from Hazelrigg nature reserve. All samples collected from the three plots are also classed as contaminated. Due to Zn being an essential trace element required by plants and animals to maintain health, the metal is subject to higher legislative guideline values than Pb. Only one sample collected from the Hazelrigg nature reserve and S. Gosforth sites exceeded the Dutch action value, with one additional sample collected from the Town Moor exceeding the HPTULT value. None of samples collected from the three plots exceeded the HPTULT value for Zn.

Despite the future persistence and hazard of heavy metals within the soil being predicted in view of their partitioning, few European countries have specified guidelines for the various metallic forms. Within the soil of plot I Pb has been shown to be less mobile than Zn, although changes in edaphic conditions (pH, organic content and CEC) may affect the relative mobility and availability, and hazard associated with the two metals. If legislation is to evaluate more fully the adverse effects of metals on human and animal health, and on the environment, environmental legislation must consider not only the total concentration but also the bioavailability of heavy metals. Considering the trend towards increasingly stringent environmental legislation, it looks likely that UK trigger thresholds will converge towards those of the Dutch system, under which an increased number of samples collected during this present study will be classed as contaminated. So in the future, areas now classed as uncontaminated may be classed as contaminated.

9.8 RECOMMENDATIONS TO MANAGERS OF POLLUTED SITES

A number of guidelines exist for use by site investigators when examining contaminated land (outlined by the ICRCL (1987)) including a list of processes that should be followed. It is essential that a site investigation commences with a desk survey involving the examination of maps and site plans in addition to collation of both historical and contemporary information regarding the site and surrounding area. This desk survey provides the investigator with:

- An insight into potential contaminants, their sources and possible forms.

- An indication of contaminant concentrations, although soil contaminants such as heavy metals are often heterogeneous varying notably over short distances and within individual samples.
- Information regarding the spatial distribution of contamination at the site, i.e. areas likely to exhibit the highest or most variable concentrations of a contaminant. These will require more detailed investigation.

However, historical information is often inaccurate or non-existent particularly when anthropogenic activities pre-date licensing laws. Identification of the exact location of pre-licensing landfill sites, for example, can be problematic.

A detailed ground examination of the site is the second stage to a site investigation, although this is usually conducted in conjunction with the desk survey. Examination of a site with a degree of prior knowledge regarding past and present disturbances aids in identification of certain features. An assessor with a degree of knowledge about a site will gain far more insight when examining a site than one who has none. The site investigation enables the assessor to locate, on the ground, features identified during the desk survey, in addition to possible sources of exposure of possible contaminant(s) to human, animal and aquatic life. These include areas of bare soil with the potential to produce dust during dry conditions, nearby surface water bodies and groundwater. The potential for exposure of non-contaminated areas as direct result of contamination at the site can also be determined, although further information regarding the solubility and mobility of contaminants will be required to draw firm conclusions.

It can be difficult to identify certain features when conducting a ground survey, for example, changes in vegetation cover, however relatively in-expensive sources of information such as aerial photographs may be helpful. Changes in vegetation cover can indicate areas of high / moderate and low contamination, plant health being affected by certain contaminants. Aerial photos can be used to digitise information on vegetation cover allowing an assessor to estimate, with reasonable accuracy, the spatial scale of contaminant variation. Sampling may then be concentrated on specific areas.

The need to determine not only total concentrations but also forms of contaminants within soils has been highlighted relatively recently. It has finally been recognised

(EPA 1995 part IIA) that the existence of a contaminant at a site does not necessarily result in significant harm to humans, animals or buildings. The likelihood of harm being caused is directly related to the form of the contaminant and edaphic conditions. Exchangeable metals have been identified as the most soluble, mobile and bioavailable fraction and are therefore the best indicator of potential hazard. Research has shown however that the full exchangeable fraction is not available for plant uptake, indicating a need to examine contaminants within plants in order to assess risk to plant health, humans consuming the plants and grazing animals. To fully evaluate the risk of soil contaminants to grazing animals it is also essential to consider the quantity of soil ingested by animals whilst grazing. This factor is of particular relevance at the Nuns Moor site as cattle grazing at the site have the potential to accumulate contaminants in both milk and meat ultimately passing them along the food chain to man.

During the present study inhalation of Pb contaminated soil dust has been identified as a possible cause for concern at the Nuns Moor site. Patches of bare soil, a seasonal phenomenon, have been identified close to site access points and the small tributary draining the site. These have been associated with heavy usage, for example, trail biking and the use of the tributary by cattle for drinking. Many other contaminated sites experience similar patches of bare soil be it a result of poor vegetative growth due to the contaminated soil. It is advised therefore that site managers aim to maintain some kind of vegetation cover at such sites. Periodical movement of site access points, for example, will reduce wear on heavily used areas. Temporary fencing should be used to restrict access to areas of bare soil giving vegetation a chance to re-establish. In the case of the Nuns Moor site alternative drinking facilities must be provided for cattle, these being moved on a regular basis. At sites experiencing poor vegetation cover due to high levels of contaminants resistant plant species can be utilised, in particular phytoremediators, plants that actively accumulate high concentrations of certain contaminants and hence act to reduce contaminant concentrations within the soil. Such plants may be harvested and either incinerated prior to landfill or in the case of metal contaminants used for the recovery of metal ores. The use of such plants is increasing.

Numerous other methods of site remediation exist, although they vary in both severity and cost. Liming, also known as neutralisation, is one of the least invasive and less expensive techniques. pH has been identified as a significant factor in controlling metal

solubility and mobility with more neutral and alkaline soils exhibiting lower concentrations of the available exchangeable fraction. The addition of lime to the soil, increasing pH, is therefore an effective way of limiting metal availability. The exchangeable fraction in addition to representing those metal cations non-specifically bound to permanent sites of clay minerals also includes those bound to pH dependent sites of organic matter. The availability of these pH dependent sites is strongly effected by acidity. Lower acidity leads to a reduction in pH dependent sites the result of which is retention of soil heavy metals by stronger alternative mechanisms. Liming offers, to the managers of the Nuns Moor site, a relatively cheap method whereby levels of the potentially more hazardous exchangeable Pb fraction can be reduced. The treatment may be contained to the small area of contaminated soil at the site as well as avoiding unnecessary major disturbance at the site. Due to the high concentrations of Pb at this site, its use for the grazing of cattle and as a recreational area for children managers should seriously consider some remedial treatment.

9.9 LIMITATIONS OF THE PRESENT STUDY AND POSSIBLE AVENUES FOR FUTURE RESEARCH

This study examined the spatial variability of soil Pb and Zn concentrations at a considerably finer scale than had previously been investigated however, an insufficient number of samples were collected at the finest scale to enable anisotropy to be reliably defined within the plot. Tentative conclusions were drawn, however if given the opportunity to continue this work further samples would be collected at the finest scale. Given more time, attempts would have been made to validate the kriging model by comparison of Pb and Zn concentrations within samples collected from previously non-sampled areas within the plot and the corresponding estimates from the kriged surface. A nested sampling technique would have enabled conclusions to be drawn regarding the level of spatial dependence following the collection of fewer samples.

Despite examining associations between Pb and Zn fractions and the key soil properties thought to exert an influence on metal partitioning numerous questions regarding the effects of changing soil conditions on metal mobility and availability remain unanswered. Previous research has tended to focus mainly on relationships between

soil properties and exchangeable or total metals. In order to understand more fully the mobility and availability of Pb and Zn within the soil, more detailed research is required to examine the relationships between the metal fractions and other soil properties. Sequential extraction techniques are recognised as a valuable tool for the determination of metal partitioning however, future work is required to fully evaluate these methods, ideally with the development of a standard technique to enable comparisons to be made between studies. Attempts are being made to fully evaluate the BCR technique.

APPENDIX 1

GUIDELINE VALUES

UK

Contaminant	Planned land use	Trigger threshold (mg/kg air-dried soil)
Pb	Domestic gardens, allotments	500
	Parks, playing fields, open space	2000
Zn	Any uses where plants are grown	300

Table A1.1 ICRCL 59/83 tentative trigger concentrations (ICRCL, 1987).

NETHERLANDS

Metal	Optimum (mg/kg dry weight)	Action (mg/kg dry weight)
Pb	85	530
Zn	140	720

Table A 1.2 The new Dutch list (Contaminated land, 1996).

Soil (mg/kg dry weight)			
Substance	A	B	C
Pb	50	150	600
Zn	200	500	3000

- AReference value
- BIndicative value for further investigation
- CIndicative value for cleaning-up

Table A1.3 Dutch ABC list (Bullock and Gregory, 1991).

SWITZERLAND

Amounts of pollutants contained in air dry mineral soil (g/tonne)		
Pollutant	Total content (pseudo) 2 M HNO ₃ -extract	Soluble content 0.1 M NaNO ₃ -extract
Pb	50	1.0
Zn	200	0.5

Table A1.4 Swiss guide values for pollutants in soil (Gupta *et al.*, 1996).

APPENDIX 2

SAMPLE COLLECTION AND LABORATORY ANALYSIS

Sample collection

At each sampling site a permanent feature, such as a field boundary, was identified on the ground and on the map. This line was used to construct the sampling network. O.S. co-ordinates were used to calculate the co-ordinates of each sample point for the purpose of mapping. This approach ensured that sampling could be repeated if necessary.

The distance between sampling points was measured along a compass bearing using two methods, a 30m measuring tape for short (<5m) distances and a trundle wheel with automatic counter for longer distances. The measuring tape was graduated to the nearest mm, whilst the trundle wheel counter displayed distance to the nearest 0.1m. Measuring tapes were not used for distances of greater than 5m as accuracy may be lost due to stretching of the tape and undulations on the ground. Backtracking enabled checks to be conducted at regular intervals to ensure that sample points were being identified with reasonable accuracy. Wooden posts were inserted at intervals to aid checking and also to mark the position of plots II and III.

Care was taken in the choice of tools and containers during the sampling process. Much of the equipment used for soil sampling is constructed of metal, as physical strength is required for tasks such as digging (Bruner 1986). The use of metal equipment, however, can cause problems when sampling for metals analysis. Wherever possible stainless steel tools were used as this material is fairly inert and does not corrode. Galvanised tools were avoided as the abrasive nature of soil can cause the coatings to scrape off and enter the sample. Plastic and polythene containers are generally considered acceptable when sampling soils for metals analysis (Bruner 1986).

Once each sample point had been identified, a thin layer of turf, approximately 15cm by 15cm was removed and soil collected from the top 5cm using a trowel; this layer was

classified as topsoil. Care was taken to ensure that the trowel was cleaned between sample points. Soil samples were stored in polythene bags from which the air was removed before sealing. All samples were externally labelled using a permanent marker pen, as labels and inks can contain significant quantities of heavy metals (Rubio and Ure, 1993). Subsoil samples were collected in a similar manner from a depth of 15 – 20cm. Following sample collection excess soil and turf were carefully replaced.

Laboratory analysis

Pre-treatment and storage

Following collection, soil samples were immediately oven dried in steel trays to aid storage and homogenisation, and to minimise any speciation changes that may occur within a moist soil during storage (Ure, 1996). Once dry samples were gently ground using a porcelain pestle and mortar to break up any aggregated material and passed through a 2mm sieve to remove stones. All analyses were conducted on the less than 2mm fraction of the soil, as is normal laboratory procedure (Rubio and Ure, 1993; Ure, 1996). Care was taken to avoid cross contamination of samples and loss of fines during the grinding and sieving processes. Throughout these procedures all equipment was kept clean and any fines were carefully brushed into the appropriate sample bag. Soils were stored at room temperature in dry sealed polythene bags from which the air had been removed. Ure (1996) conducted tests on soil storage temperatures and duration and found that no significant changes in the quantity of acetic acid or EDTA extractable Pb or Zn in soils stored at –20°C, 20°C and 40°C over a 12 month period. Storage of dry soils at normal room temperature was therefore considered appropriate for this study.

Heavy metal extraction

Total metals (Mellor and Bevan, 1999)

0.5g \pm 0.01g of < 2mm air dried, ground and homogenised soil was weighed into PTFE microwave digestion vessels (Figure A2.1). The vessels were placed in a fume cupboard and 3ml of nitric acid added. The vessels were allowed to stand for 30minutes before 9ml of hydrochloric acid and 8ml of distilled water were added. The safety valves and caps were applied to the correct torque, using the capping station.

Venting tubes were fitted and the samples microwaved using a CEM, MDS 81D microwave, following the programme specified in Table A2.1.

The samples were allowed to cool in a fume cupboard before filtering through 5cm diameter quartz filter papers. The filtrate was made up to 100ml with distilled water and stored until analysis.

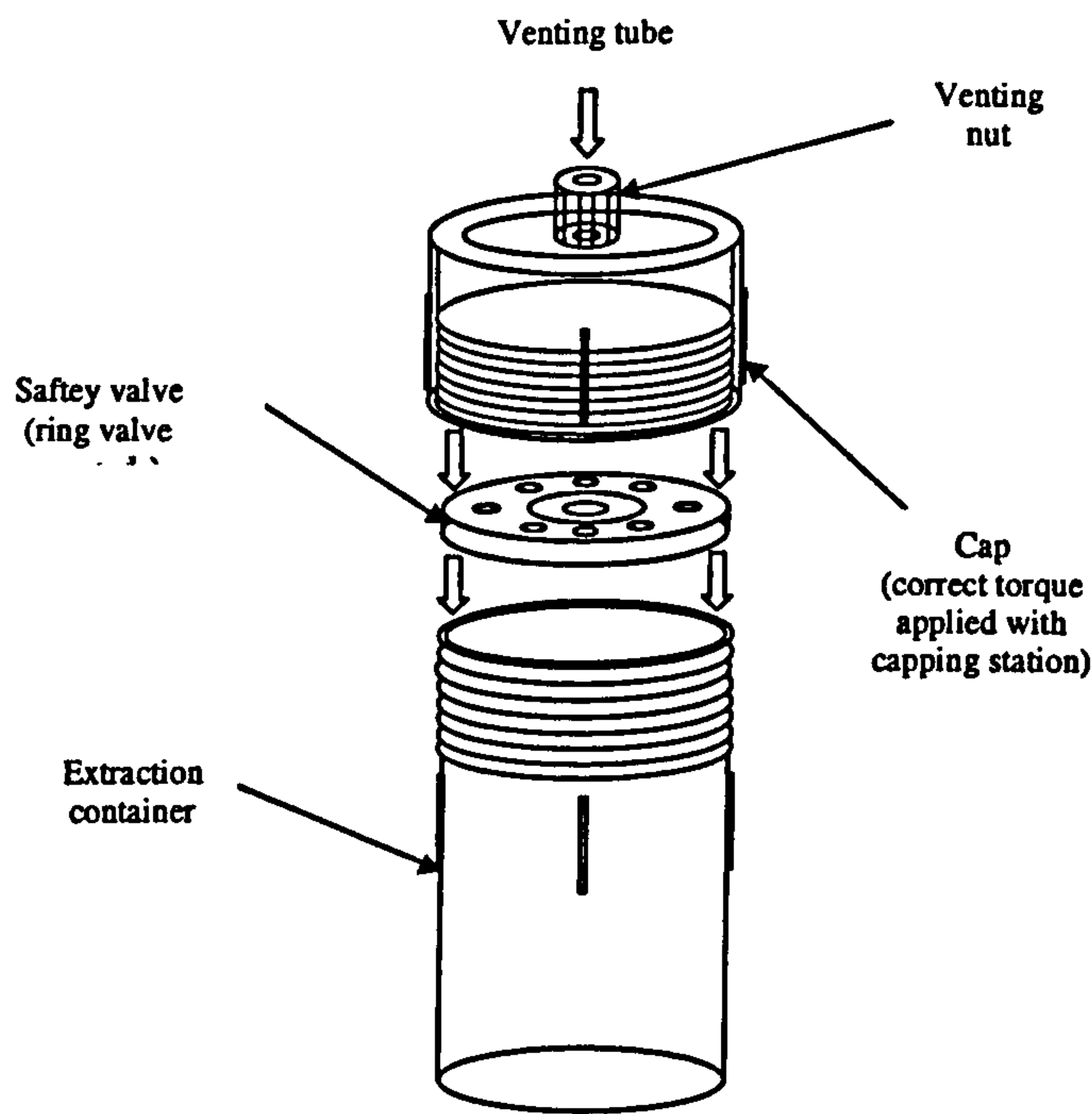


Figure A2.1 Diagram of microwave digestion vessel, showing assemblage.

stage	power (%)	time (mins)
1	100	2.00
2	65	43.00
3	0	15.00

Table A2.1 Microwave digestor programme (12 containers)

Sequential extraction (Davidson *et al.*, 1994)

The chosen sequential extraction technique separated the metals into 4 different forms: exchangeable (water and acid soluble), reducible (e.g. attached to iron or manganese oxides), oxidisable (e.g. attached to organic matter and sulphides) and residual, using a series of increasingly strong reagents (Table A2.2). The final stage, involving extraction of the residual metal fraction utilised the microwave digestion method outlined for total metal extraction. A total of 5days were required to extract all 4 forms of metals from the soil.

	step	fraction	reagents
increasing strength ↓	1	exchangeable	0.11 M Acetic acid
	2	reducible	0.1 M Hydroxylammonium chloride (adjusted to pH 2 with nitric acid)
	3	oxidisable	8.8 M Hydrogen peroxide
	4	residual	1.0 M Ammonium acetate (adjusted to pH 2 with nitric acid) Hydrochloric acid Nitric acid

Table A2.2 Summary of the reagents used and the metal fractions extracted by the sequential extraction method.

Step1 – Exchangeable (water and acid soluble): 1g ± 0.001g of soil was weighed into a 100ml polypropylene centrifuge tube. 40ml of 0.11M acetic acid was added, and the suspension shaken in a wrist action shaker for 16hours. The suspension was centrifuged at 4000rpm for 10minutes to separate the liquid from the solid residue, and the liquid transferred into a polyethylene storage container. The extractant was stored at 4°C until analysis.

Rinsing: 20ml of distilled water was added to the residue. The suspension was shaken for 15minutes before being centrifuged at 4000rpm to separate the solid and liquid fractions. The washings were discarded. This process constituted a washing procedure and was conducted following each step of the extraction.

Step 2 - reducible (e.g. iron / manganese oxides): 40ml of 0.1M hydroxylammonium chloride, adjusted to pH 2 with nitric acid, was added to the washed residue from step 1. The suspension was shaken for 16hours in a wrist action shaker before being centrifuged to separate the solid residue from the extractant. The liquid was decanted

into a polyethylene storage container and stored at 4°C for analysis. The solid residue was then rinsed as before.

Step 3 - oxidisable (e.g. organic matter and sulphides): In small aliquots, 10ml of 8.8M hydrogen peroxide was carefully added to the washed residue from step 2. The centrifuge tube was covered with a watch glass and the contents allowed to digest at room temperature for 1hour. The tube was occasionally shaken manually. The tube was heated to 85°C in a water bath for 1hour to continue the digestion before the watch glass was removed and the contents of the tube allowed to reduce to 1 – 2ml. A second 10ml aliquot of hydrogen peroxide was added and again the tube was covered and heated to 85°C for 1hour. The volume was allowed to reduce as before. Once reduced the moist residue was allowed to cool and 50ml of 1.0M ammonium acetate, adjusted to pH 2 with nitric acid, added. The suspension was shaken for 16hours in a wrist action shaker before being centrifuged at 4000rpm for 10minutes to separate the liquid and the solid residue. The extractant was transferred into a polyethylene container and stored at 4°C for analysis. The residue was rinsed as before.

Step 4, residual: Residual metals were extracted from the solid residue from step 3 following the same technique as the total metal extraction. The digestion was started in the centrifuge tubes, to which both the nitric and hydrochloric acids were added to create a suspension. The suspension was carefully transferred into the appropriate digestion vessel and the 8ml of distilled water used to rinse the centrifuge tube before being added to the digestion vessel. The digestion was conducted as before.

Heavy metal analysis

Flame AAS

The manufacturer's instructions were followed for the set up of the AAS (Perkin Elmer, 1988). Prior to usage the lamp was allowed to heat up for a minimum of 1 hour as this was seen to produce more stable readings. The burner was also cleaned following the manufacturers programme, i.e., the aspiration of 1% nitric acid, 1M acetic acid, acetone and distilled water for 5minutes each.

The correct lamp, wavelength and slit width were selected according to the metal to be analysed and the AAS optimised (Table 4.4). Optimisation involves the maximisation of the lamp energy via vertical and horizontal alignment and fine adjustments to the wavelength. After ignition of the burner, conditions were further optimised by the adjustment of fuel flow, sample aspiration rate and burner alignment in order to maximise the absorbance of a standard known to produce 0.2 absorbance units when aspirated (Appendix 4). Once maximised the AAS was auto zeroed on a blank solution with the same matrix as the samples to be measured, and calibrated using the 3 standards. Distilled water was aspirated between standards and samples to ensure that all traces of the previous samples had been erased.

Soil properties

Soil pH (Rowell, 1994; Mellor and Bevan, 1999)

10g \pm 0.1g of soil was weighed into a 100ml glass beaker and 25ml of distilled water added. The suspension was stirred thoroughly and allowed to stand for 30minutes. Soil pH was determined using a Jenway 3020 pH meter, calibrated using standard buffer solutions of pH 4.0 and 7.0. The electrodes were inserted into the suspension, which was gently swirled and the pH level recorded once the reading had stabilised, after approximately 30seconds. The pH meter was re-calibrated at regular (c. 30min.) intervals. The process was repeated replacing the distilled water with a 0.05M CaCl₂ salt solution. The difference in pH measurement using the two solutions is known as the salt effect and is calculated using Eq. A2.1. Δ pH, the change in pH, is positive in soils with a net positive charge and negative in soils with a net negative charge.

Soil pH	$\Delta pH = pH_{water} - pH_{salt}$	Eq. A2.1
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Organic matter content – loss on ignition (Rowell, 1994; Mellor and Bevan, 1999; BBSS application method P002, no date)

Approximately 5g (W_1) of oven dry soil was weighed into a small pre-weighed crucible (W_2) and placed into a muffle furnace pre-heated to 800°C. An initial step of heating the soils to 105°C overnight to remove free water, as specified by the BBSS method, was not included as the samples had already been oven-dried. Samples were heated in

the furnace for 30minutes before being removed and allowed to cool in a desiccator, once cool they were re-weighed (W_3). The organic matter content was calculated using the Eq. A2.2 below.

Organic matter content (%)

$$O.M. = \frac{(W_2 - W_3)}{W_1} \times 10 \quad \text{Eq. A2.2}$$

Cation exchange capacity (Rowell, 1994)

Step 1: $5g \pm 0.05g$ of soil was weighed into a centrifuge bottle and the weight of the container and soil noted (M_1). 200ml of a buffered solution of barium chloride (equal volumes of (1) Triethanolamine solution, 90ml diluted to 1l, adjusted to pH 8.1 by the addition of approximately 140ml of 2M HCl and further diluted to 2l and (2) $BaCl_2$, 244g/l) was added and the suspension shaken overnight on a side to side shaker. The suspension was centrifuged for 10minutes at 3500rpm and the supernatant liquid discarded. 200ml of distilled water was added and the suspension shaken for 20minutes to break up the soil cake. The suspension was again centrifuged and the supernatant liquid discarded. The weight of the centrifuge bottle and its contents were recorded (M_2). 100ml of $MgSO_4$ was transferred into the centrifuge bottle and shaken for 2hours on a side to side shaker. Again the suspension was centrifuged at 3500rpm for 10minutes before the supernatant liquid was decanted into a labelled storage container. The liquid was refrigerated at $4^\circ C$ until analysis.

Step2, titration: 5ml of the liquid was transferred into a volumetric flask, using a pipette, and 6 drops of NH_4OH (140ml/l, 30% w/w NH_3) and 2 drops of freshly prepared omega chrome black indicator solution (VS 0.1%) added. The solution was titrated with EDTA solution (EDTA – disodium salt, 3.723g/l) until the end point was reached, i.e. a colour change from pink through clear to blue. The volume of EDTA solution (A_1) required to reach the end point was recorded. A 5ml sample of $MgSO_4$ solution was titrated similarly and the end point volume (B) noted. After correction for the effect of the volume of liquid retained by the soil after decanting (Eq. A2.3), the cation exchange capacity (CEC) was calculated using Eq. A2.4.

Titration (corrected) (ml)

$$A_2 = \frac{A_1(100 + M_2 - M_1)}{100}$$

Eq. A2.3

Cation exchange capacity (me/100g)

$$CEC = 8(B - A_2)$$

Eq. A2.4

APPENDIX 3

QUALITY CONTROL: NON-STANDARD HEAVY METAL EXTRACTION TECHNIQUES

Heavy metal extraction

Quality checks were conducted to assess the reproducibility and efficiency of the two metal extraction techniques prior to initiation of the sampling programme. The checks were conducted using sub-samples from a test soil sample, a single large sample collected from the Town Moor in Newcastle upon Tyne, and a standard reference soil (SRS) (ORM Laboratory of the Government Chemist, ref no. GBW07406) of known metal concentration. The techniques were tested at the 95% level; 95%, or more, of the sub-samples were required to display Pb and Zn concentrations within ± 2 s.d. of the overall mean.

Microwave extraction

Reproducibility

Total metals (Pb and Zn) were extracted from approximately 60 sub-samples of the test soil using the technique outlined in Appendix 2. The sub-samples were extracted in batches of 11, the 12th sample being replaced by a blank containing no soil. Blanks were included to confirm that samples were not being contaminated during the extraction process. The use of control samples identified a problem with Zn contamination, which was traced to the glass fibre filter papers used to filter the extractant. No contamination was detected when quartz papers were used.

The sub-samples exhibited a wide range of Pb and Zn concentrations, varying between 218 – 283mg/kg and 194 - 375mg/kg, respectively. The microwave technique determined that the bulk sample contained on average 249mg/kg of Pb and 304mg/kg of Zn (Table A3.1). The concentrations were approximately normally distributed (Figure A3.1). The data were tested for normality using the method described by Gregory (1978). This author states that a data set which approximates to the normal frequency distribution will fit or fall close to a straight line when its cumulative probability function is plotted on probability paper. The closer the points are to a straight line the

better the approximation to the normal distribution. 95% and 97% of the sub-samples exhibited Pb and Zn concentrations within 2s.d. of the mean indicating that the extraction method was reproducible. It was noted that the data set exhibited a large standard deviation, indicating high levels of variability within the bulk sample.

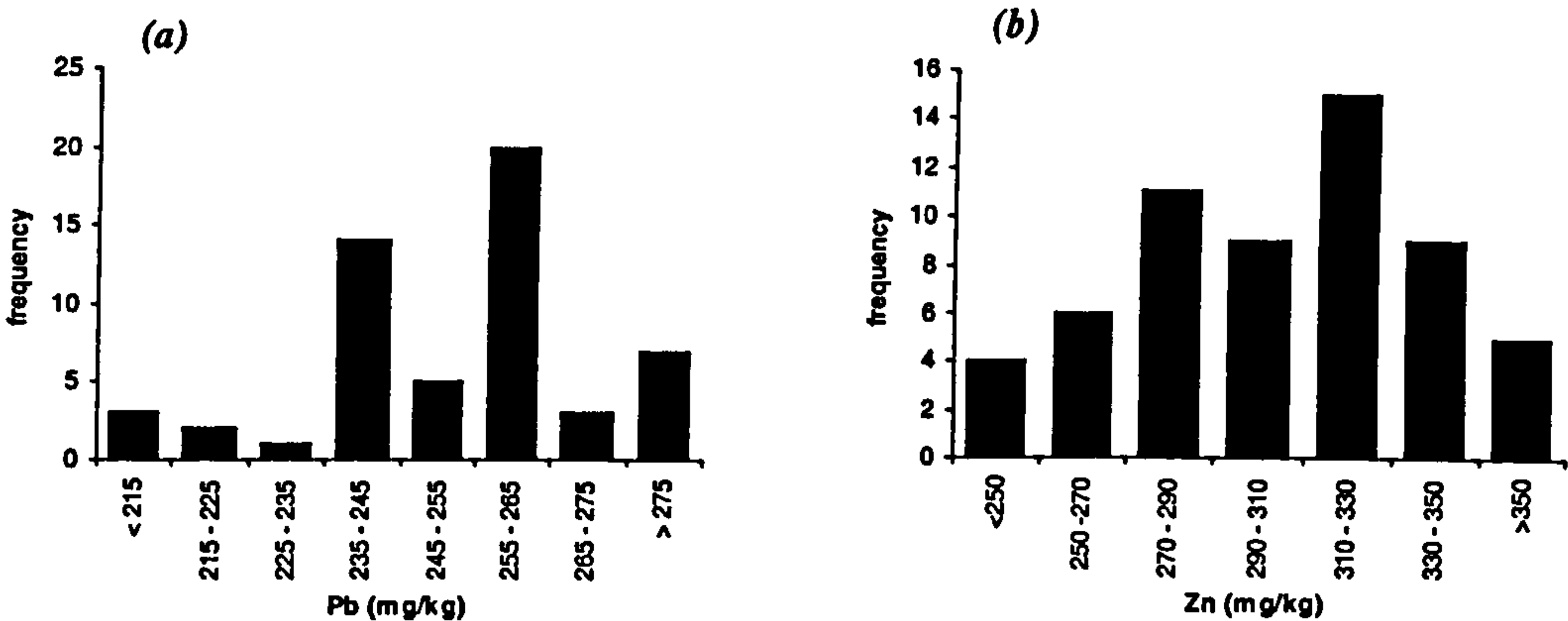


Figure A3.1 Reproducibility of microwave digestion technique, (a) Pb, (b) Zn

metal	n	mean	s.d.	min	max	%
Pb	53	249	15	217	283	95
Zn	58	304	36	194	375	97

Table A3.1 Variation in concentrations of Pb and Zn within sub-samples of the test soil, extracted using the microwave technique. % indicates the proportion of sub-samples for which the Pb and Zn concentrations fell within 2 s.d. of the mean. Units given are mg/kg.

Efficiency

The extraction efficiency, the % of the total metal extracted using the microwave technique, was evaluated using a standard reference soil (SRS) of known metal concentration. Two batches of 10 sub-samples, 1 test soil and 1 blank sample were extracted and analysed as before and the metal concentrations compared to those quoted by the suppliers.

The sub-samples taken from the SRS exhibited a lower degree of variation than those taken from the test soil, due to better homogenisation within the SRS. Any observed variation could therefore be attributed to the extraction and analysis processes. On

average the microwave extraction technique determined that the SRS contained 314mg/kg of Pb and 88mg/kg of Zn, with only a minor variation noted (Table A3.2). Figure A3.2 demonstrates the level of variation between the sub-samples, displaying graphically the relationship between the measured concentrations of Pb and Zn and the known levels within the SRS. Error bars represent the variation in metal concentration measured using AAS. Each error bar represents ± 2 standard errors of the mean (2SEM). The microwave technique extracted on average 100% and 92% of total Pb and Zn, respectively (Table A3.2), exhibiting comparable sub-sample variation to that specified by the suppliers. The technique was accepted as being both reproducible and efficient.

element	n	Mean (μ_e)	2SEM _e	$\mu \pm 2SEM_k$	% efficiency
Pb	20	314	2.7	314 ± 6	100
Zn	20	88	1.5	97 ± 2	92

Table A3.2 Efficiency of the microwave extraction technique. e – extracted metals, k – known level (as specified by the suppliers). 2SEM – 2 standard errors of the mean. (unit mg/kg)

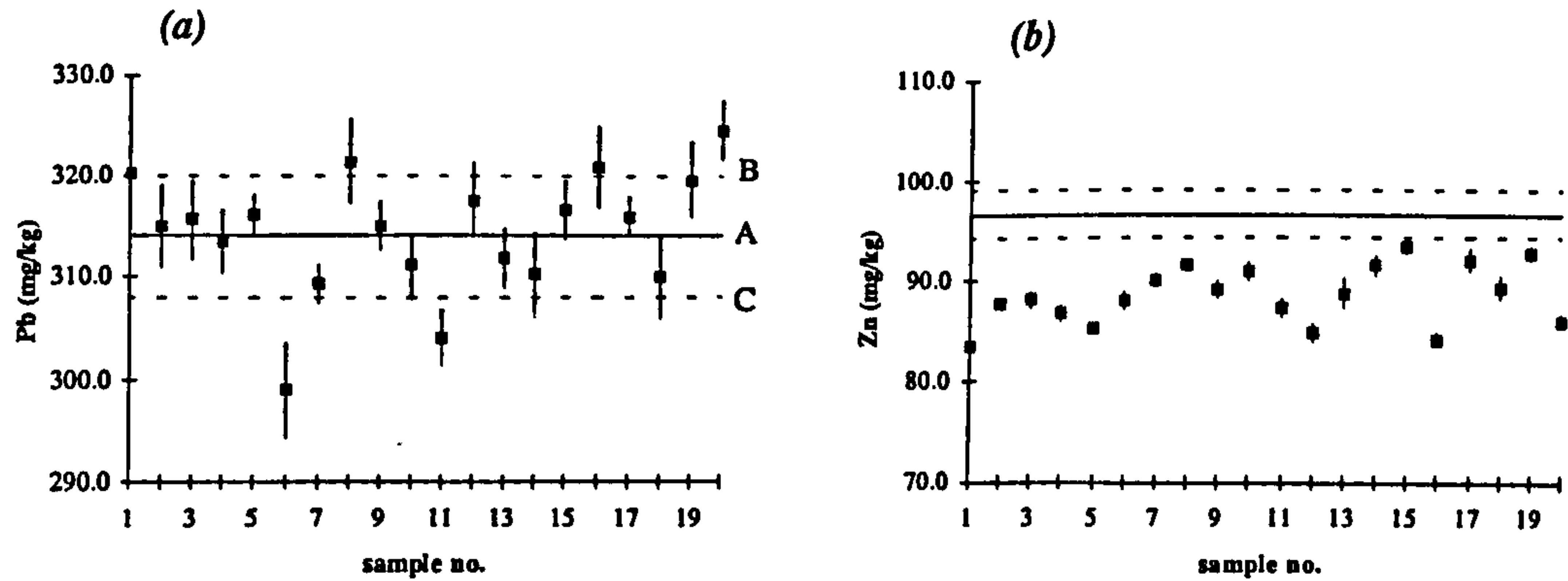


Figure A3.2 Variation in metal concentrations extracted from SRS using the microwave technique, (a) Pb and (b) Zn. The known concentrations of metals within the SRS are indicated by the lines, A: mean concentration, B: + 2SEM, C: - 2SEM.

Sequential extraction: BCR technique

Reproducibility

Metals were extracted from 28 sub-samples of the test soil using the sequential extraction method specified in Appendix 2. Each sub-sample was separated into 4

metallic forms (exchangeable, reducible, oxidisable, and residual). For each stage of the extraction the Pb and Zn concentrations within the sub-samples were assessed for reproducibility. As with the total metals, 95% of the samples were required to display metal concentrations within 2s.d. of the mean as well as showing a normal distribution. Figures A3.3 and A3.4 show the distribution of Pb and Zn concentrations extracted by

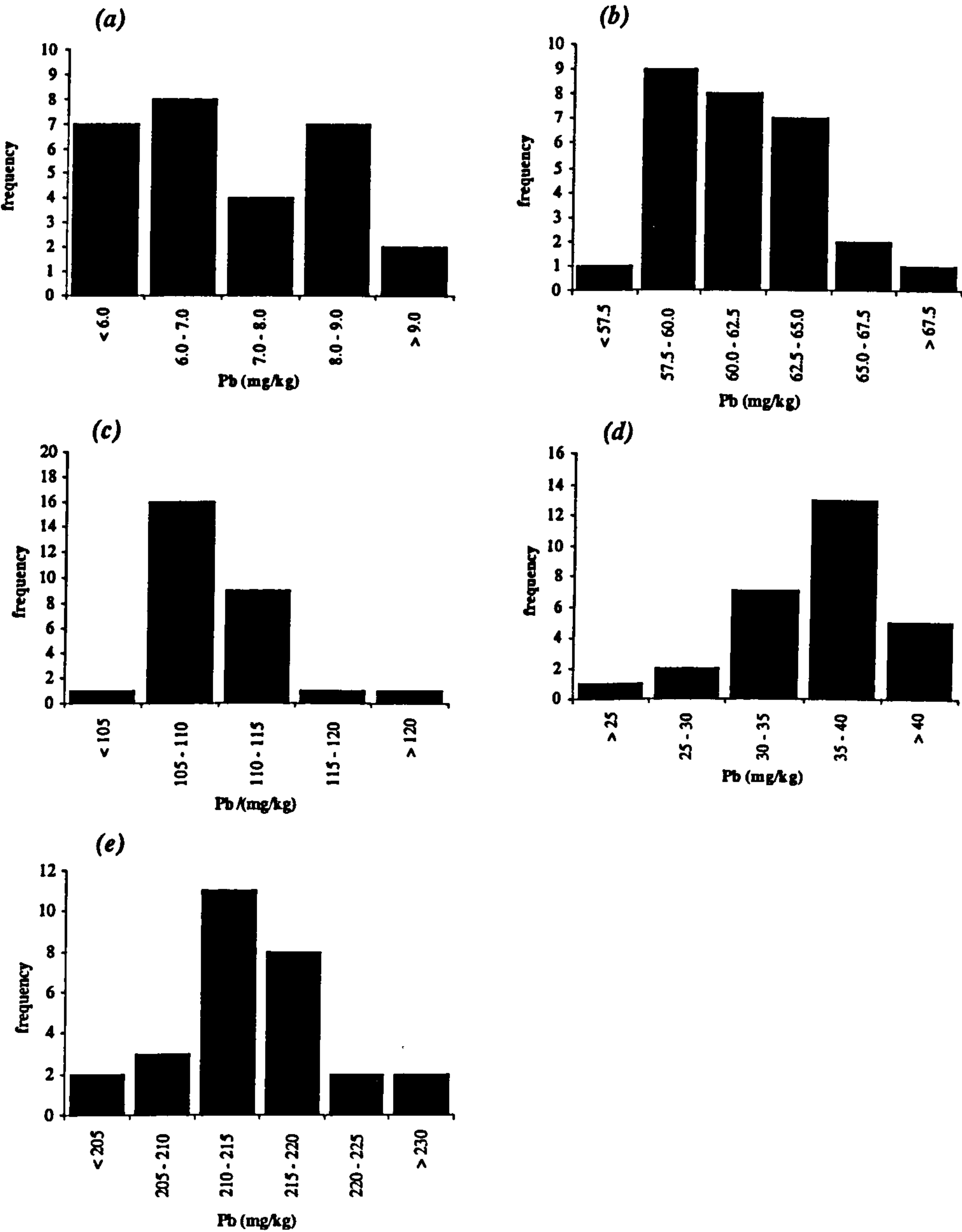


Figure A3.3 Reproducibility of the sequential extraction technique for the extraction of Pb.
(a) step 1: exchangeable; (b) step 2: reducible; (c) step 3: oxidisable; (d) step 4: residual;
(e) total – sum of the fractions

each stage of the sequential extraction; a summary of the results is displayed in Table A3.3. The quantity of metal extracted in each fraction was summed to give the total concentration within each sub-sample. At each stage of the extraction, the technique was found to be reproducible for both Pb and Zn.

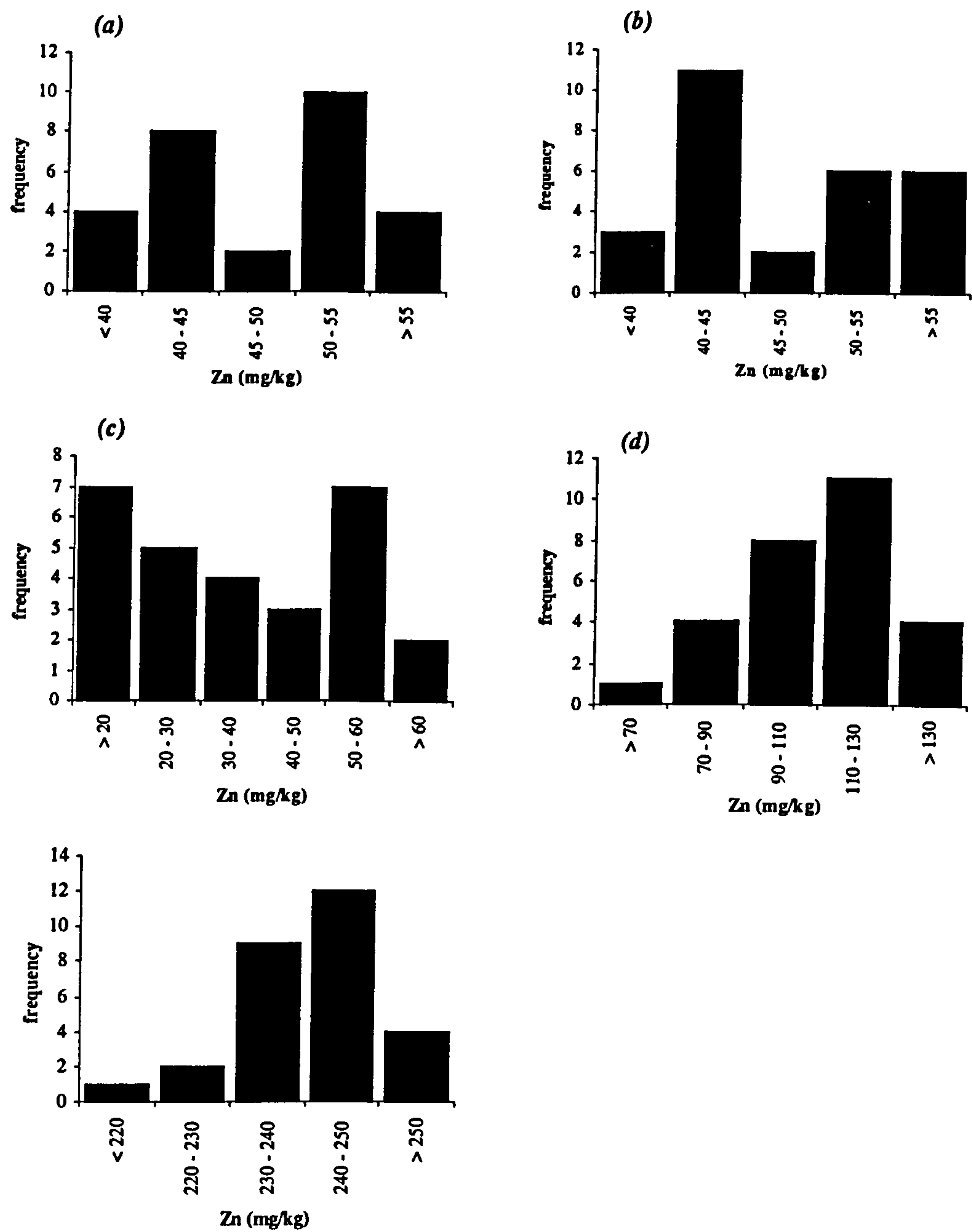


Figure A3.4 Reproducibility of the sequential extraction technique for the extraction of Zn.
(a) step 1: exchangeable; (b) step 2: reducible; (c) step 3: oxidisable; (d) step 4: residual;
(e) total – sum of the fractions

step	Pb			Zn		
	mean (mg/kg)	s.d.	reproducibility (%)	mean (mg/kg)	s.d.	reproducibility (%)
1	7	1.2	100	48	7.2	100
2	62	3.1	96	48	6.5	100
3	111	5.3	96	36	16.0	100
4	36	4.7	93	108	17.7	96
total	215	5.7	96	240	11.0	96

Table A3.3 Variation in concentration of Pb and Zn within the test soil, extracted using the sequential extraction technique. % reproducibility, indicates the proportion of sub-samples for which the Pb and Zn concentrations fell within 2 s.d. of the mean.

Efficiency

The sequentially extracted sub-samples displayed total mean concentrations of 215mg/kg and 240mg/kg for Pb and Zn, respectively, with values ranging from 203 – 229mg/kg and 207 - 263mg/kg. The test soil was known to contain on average 249mg/kg of Pb, extracted at 100% efficiency, and 304mg/kg of Zn extracted at 92% efficiency. The sequential extraction procedure was therefore calculated to be 86% and 73% efficient at extracting Pb and Zn, respectively (Table A3.4).

element	mean (mg/kg)	extraction efficiency (%)	mean (mg/kg)	extraction efficiency (%)
Pb	249	100	215	86
Zn	304	92	240	73

Table A3.4 Efficiency of sequential extraction technique.

PAGE

NUMBERING

AS ORIGINAL

The variation of k with wavelength is normally distributed, hence for wavelengths close to the absorption maximum k displays little variation. k may therefore be taken as constant if the range of wavelengths over which absorbance is measured is small and centred around the maximum wavelength for the absorption profile. The concentration of atoms within the vapour, i.e. the number of atoms per unit volume, C , is directly proportional to the radiation absorbance, A , and inversely proportional to K , a constant, and L , the path length through the atomic vapour (Eq. 3).

$$C = \frac{A}{(KL)} \quad \text{Eq. 3}$$

Instrumentation

A diagram of a single beam atomic absorption spectrometer is shown below (Figure A4.2). It consists of four main components, a sharp line radiation source, a solution nebuliser, a monochromator and an amplifier and recording system.

- The **sharp line radiation source**, a hollow cathode lamp, contains a cathode of the same element as is to be analysed. It therefore radiates only light of wavelengths the element may absorb. The lamp emits discrete wavelengths, the spectral lines of which are narrower than the absorption lines being measured. A narrow slit may be used to isolate an individual emitted wavelength thus reducing the need for high resolution.
- The **solution nebuliser** disperses the sample solution into a fine aerosol via high velocity impact with a glass bead before vaporisation by a **flame**.
- The **monochromator** isolates the absorption line from background light present due to interferences and controls the intensity of transmitted light reaching the **detector**.
- An **amplifier** and a **recording system** to amplify and record the signal.

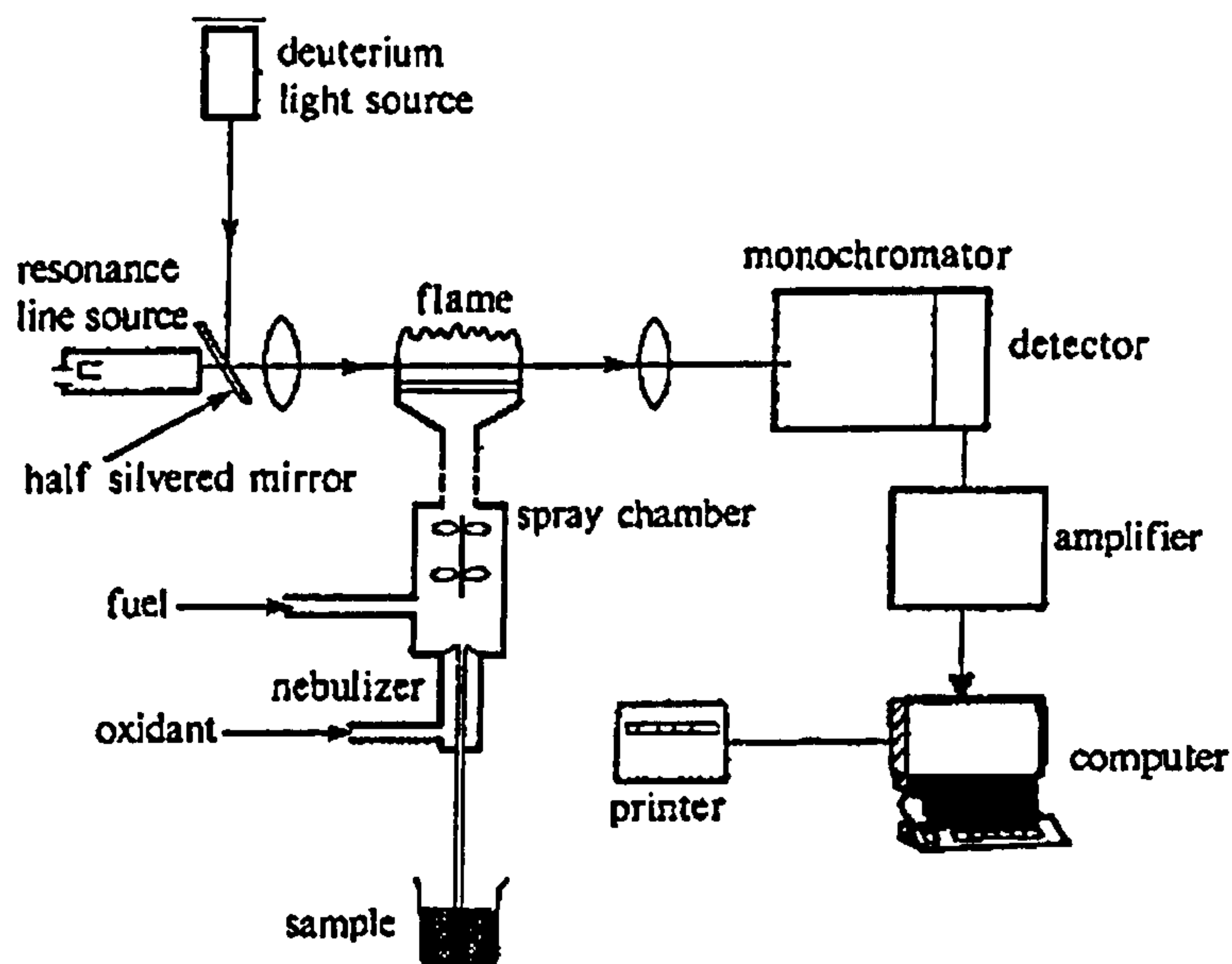


Figure A4.2 Flame atomic absorption system (Source: Fifield and Kealey, 1995).

Calibration and optimisation

The concentration of atoms within the light path is affected by several operating factors causing the sensitivity of the instrument to vary. Sensitivity should be maximised prior to instrument calibration and analysis. Instrument sensitivity is measured by the aspiration of a solution of concentration known to produce an absorbance signal of 0.0044 absorbance units, the equivalent of a 1% decrease in radiation. In practice, this absorbance is very small so when optimising a greater concentration is used. For example, an absorbance of 0.0044 absorbance units is obtained for a sample containing 0.1ppm of Pb, and an absorbance of 0.440 absorbance units is obtained for a sample containing 10.0ppm of Pb. Sensitivity may be affected by the factors listed below (Table A4.1).

The instrument is calibrated via the aspiration of known standards, from which a graph of concentration vs. absorbance may be generated. At low absorbance values calibration graphs are generally linear but due to interference effects curve towards the concentration

axis at higher concentrations (Figure A4.3). A lower degree of accuracy is obtained on the curved section of the graph, where a small change in absorbance produces a large change in concentration. Samples falling outside the range of the calibrating standards must be diluted as extrapolation of the curve can lead to inaccuracies. Measurements may be made within the concentration range 0.1ppm - 100ppm with between 0.5% and 2% precision.

Factor	Solution
<ul style="list-style-type: none">• Sample viscosity, affecting sample uptake flow rate.• Incorrect alignment of flame in light path• Incorrect flame condition.• Interferences	<p>Adjustment of nebuliser, to alter sample aspiration rate.</p> <p>Adjustment of vertical, horizontal and rotational controls of the burner.</p> <p>Adjustment of the fuel, oxidant mixture.</p>
<p>Emission - emission of the element at the same wavelength as that at which absorption is occurring.</p> <p>Chemical - prevention or suppression of the formation of ground state atoms.</p> <p>Matrix - enhancement or depression of sensitivity.</p>	<p>Increasing the radiation source current, or reducing the slit size.</p> <p>Addition of a suitable reagent to aid in the release of the cations, or the use of higher temperatures.</p> <p>Standard additions or matrix matching of samples and standards.</p>

Table A4.1 Some problems commonly encountered during AAS analyses and possible solutions (Information from Fifield and Kealey, 1995)

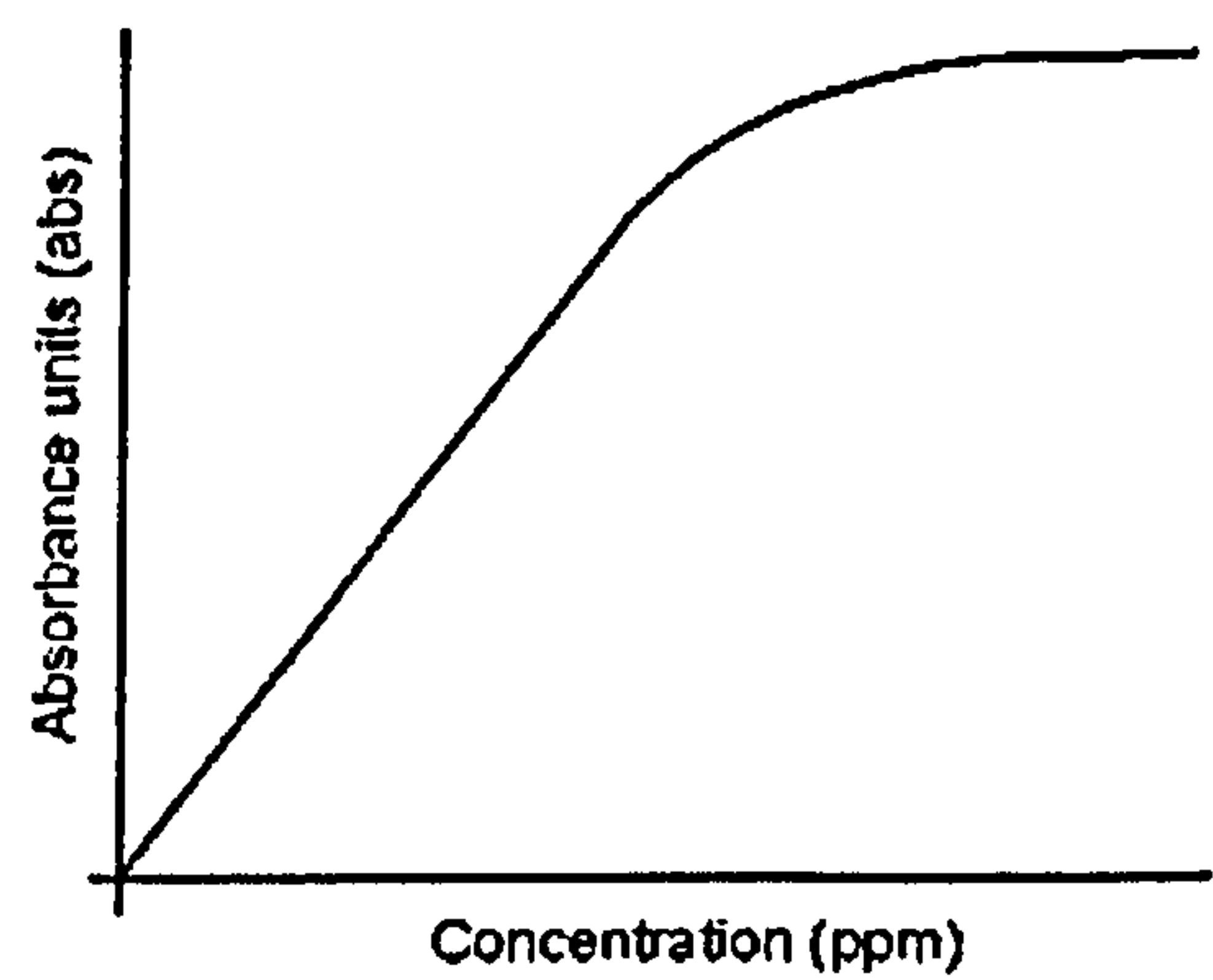


Figure A4.3. Variation of adsorbance with metal concentration.

APPENDIX 5

SPATIAL DEPENDENCE

Introduction

Spatial dependence defined as ‘the propensity of a variable to exhibit similar (or different) values as a function of the distance between the spatial locations at which it is measured’. It is one element of a broad domain known as geostatistics, a group of tools aimed at exploring spatial information (Environmental Modelling: spatial dependence, no date). Geostatistical techniques were first developed in the 1960s for use in the mining industry, fulfilling an ultimately economic need to improve estimates of ore concentrations. The techniques have since played an important role within geo-sciences (Elements of Geostatistics, no date). Two individuals particularly closely involved in their development were Matheron, responsible for development of the theory and Krige, who further developed and applied the theory empirically (Webster and Oliver, 1990). Geostatistics provides tools for:

- Examining and describing the variation / spatial structure of a property over the earth’s surface.
- Accurately estimating the attributes / values of a property at non-sampled locations, in other words, accurate interpolation.
- Designing / determining efficient / optimum sampling schemes.

(Webster and Oliver, 1990; Environmental modelling: spatial dependence, no date)

Theory / assumptions

The majority of soil properties vary continuously over space, thus there is a tendency for samples taken closer together to be more similar than those taken further apart. The properties of individual samples are therefore seen to be dependent upon each other and may in theory be described by a statistical function. In practice, this variation can be very irregular, requiring complex equations to describe it. Such properties, known as *regionalized variables*, must hence be regarded as random variables and their variation over space examined statistically (Webster and Oliver, 1990).

The relationship between a certain property measured at two places some distance apart may be described by its variance; this is considered the most suitable tool as it is least affected by sampling fluctuations. If a property (Z) has been measured at several points along a transect or vector, with each point separated by a known distance or lag (h), then an average semi-variance or variance (s^2) can be calculated for that lag, using Eq. 1. Where m is the number of pairs separated by lag h (Webster and Oliver, 1990).

$$s^2 = \frac{1}{2m} \sum_{i=1}^m \{z(x_i) - z(x_i + h)\}^2 \quad \text{Eq. 1}$$

The concept of *stationarity* must be adhered to if the description of variation is to be extended from the data set to the whole population. The concept assumes that at any position a property, Z , is a random variable, and hence its value may be one of many values generated by a random process (Webster and Oliver, 1990). The mean and variance of the variable must be constant throughout the sampled area (Environmental Modelling: spatial dependence, no date). An expectation may therefore be assigned to the property, Z , at x ; this value is constant and is not affected by the position of x . The expected value is the mean (μ) (Eq. 2), and the variable is said to be *stationary to the mean* when this assumption holds (Webster and Oliver, 1990).

$$E[z(x)] = \mu \quad \text{Eq. 2}$$

The variance of the differences between pairs must also be stationary for any lag. Hence the expected squared difference between values at places separated by the lag, h , must be finite and depend only on h (Eq. 3) (Webster and Oliver, 1990).

$$E[\{z(x) - z(x + h)\}^2] = 2\gamma(h) \quad \text{Eq. 3}$$

$\gamma(h)$ is the expectation of s^2 , the semi-variance, at lag h . γ depends on h , the two being related by a function known as the semi-variogram or variogram which is used to describe the *spatial correlation / similarity* between variables (Environmental Modelling: spatial dependence, no date).

The variogram is a measure of half the average squared difference or semi-variance between pairs of data values separated by given distances, lags, on the ground

(Environmental Modelling: spatial dependence, no date). The graph can easily be computed from a set of measurements made along a transect at regular intervals and is conducted by calculating the average semi-variance for any integral multiple of the sampling interval (Figure A5.1), i.e. $\gamma(h)$, $\gamma(2h)$, $\gamma(3h)$, $\gamma(nh)$, using the generalised equation below (Eq. 4) (Webster and Oliver, 1990; Oliver and Webster, 1991; Kaluzny *et al.*, 1998).

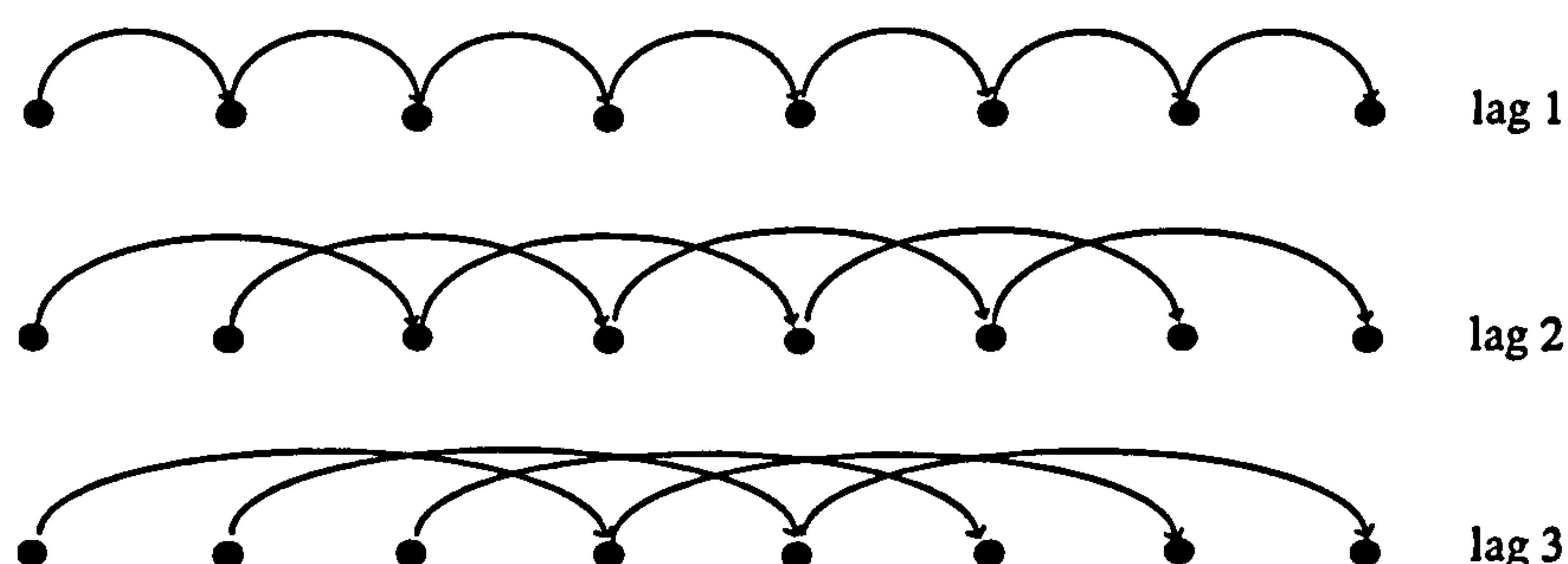


Figure A5.1 Diagrammatic illustration of lag separation
(adapted from webster and Oliver, 1990)

$$\gamma(h) = \frac{1}{2(n-h)} \sum_{i=1}^{n-h} \{z(i) - z(i+h)\}^2 \quad \text{Eq. 4}$$

For a regular grid, this theory may easily be extended to 2 dimensions (Webster and Oliver, 1990).

In general, the larger the number of samples the more accurately the semi-variances may be estimated. The formulae are highly sensitive to skewed data, but may be used on non-normally distributed data provided that it may be easily transformed to normality (Webster and Oliver, 1990). Variograms should in general be limited to a maximum lag distance equal to half the sampled distance, in addition to a minimum of 30 pairs being used (Journel and Huijbregts, 1978; Variograms, no date).

The idealised variogram will rise as lag distance increases, before levelling off or stabilising at a particular semi-variance (Figure A5.2). This levelling is known as the

sill, and the lag at which it is reached, the range. The range is the limit to spatial dependence; beyond this distance, samples are no longer correlated and are independent (Journel and Huijbregts, 1978; Isaaks and Srivastava, 1989; Webster and Oliver, 1990; Oliver and Webster, 1991; Environmental Modelling: spatial dependence, no date; Variograms, no date).

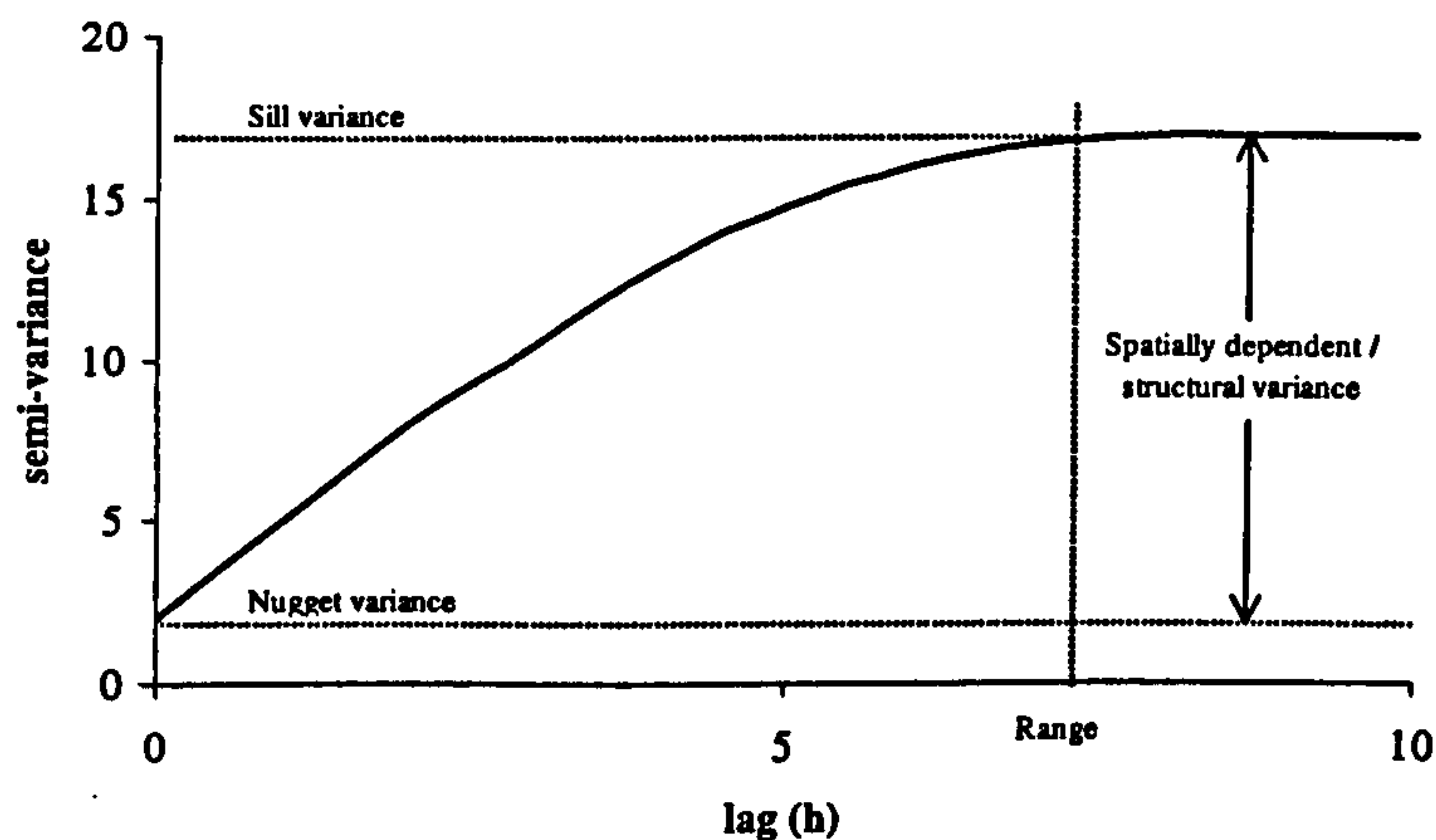


Figure A5.2 Idealised semi-variogram, indicating main features

By definition, the semi-variance at lag = 0 is zero as a pair of measurements made at the same spatial location should yield the same value. In practice, however, it is often the case that the semi-variance is positive (Figure A5.2). This is known as the nugget variance and is caused by component variation at $h = 0$ (Webster and Oliver, 1990; Spatial statistics, no date; Variograms, no date). The phenomenon, named the nugget effect, may arise due to, (1) measurement error (operator error and inaccuracies in the measuring device) or (2) the spatial dependence of the property occurring over a much smaller scale than the shortest sampling interval (Woperies *et al.*, 1988; Webster and Oliver, 1990; Environmental Modelling: Spatial dependence, no date). In extreme cases all the variation appears to be nugget; here the nugget variance represents the sill variance of a small scale structural component. In these cases the actual shape of the variogram can only be fully determined by denser sampling.

Typically 2 dimensional variograms exhibit directionality, i.e. they vary according to the direction of the transects along which a property has been sampled (Environmental Modelling: spatial dependence, no date). This non-coincidence of variograms is known

as anisotropy and is checked for by constructing variograms for a minimum of 3 / 4 directions (Webster and Oliver, 1990; Variograms, no date). By convention, these directions are: N/S, E/W, NW/SE and NE/SW. Anisotropy may be geometric, when directional variograms exhibit the same sill but different ranges of the same model, or zonal, when variograms exhibit either different models or sills. Geometrical anisotropy may be removed via the use of a linear transformation. Removal of zonal anisotropy, on the other hand, requires either the de-trending of the data or use of a nested variogram model (Kaluzny *et al.*,1998; Variograms, no date).

Variogram models may be divided into two main types: (1) bounded models which stabilise around a sill and have a finite variance, and (2) non-bounded models without a sill which appear to increase indefinitely (Webster and Oliver, 1990; Variograms, no date). Models may be fit by eye or using the method of least squares, and must describe a minimum of three variogram features, an intercept on the y-axis, the increase in the semi-variance and a sill (Webster and Oliver, 1990). The main models are displayed below (Figure A5.3), and may be used individually, or in some cases combined where a variogram is more complex, thus requiring a more elaborate nested model.

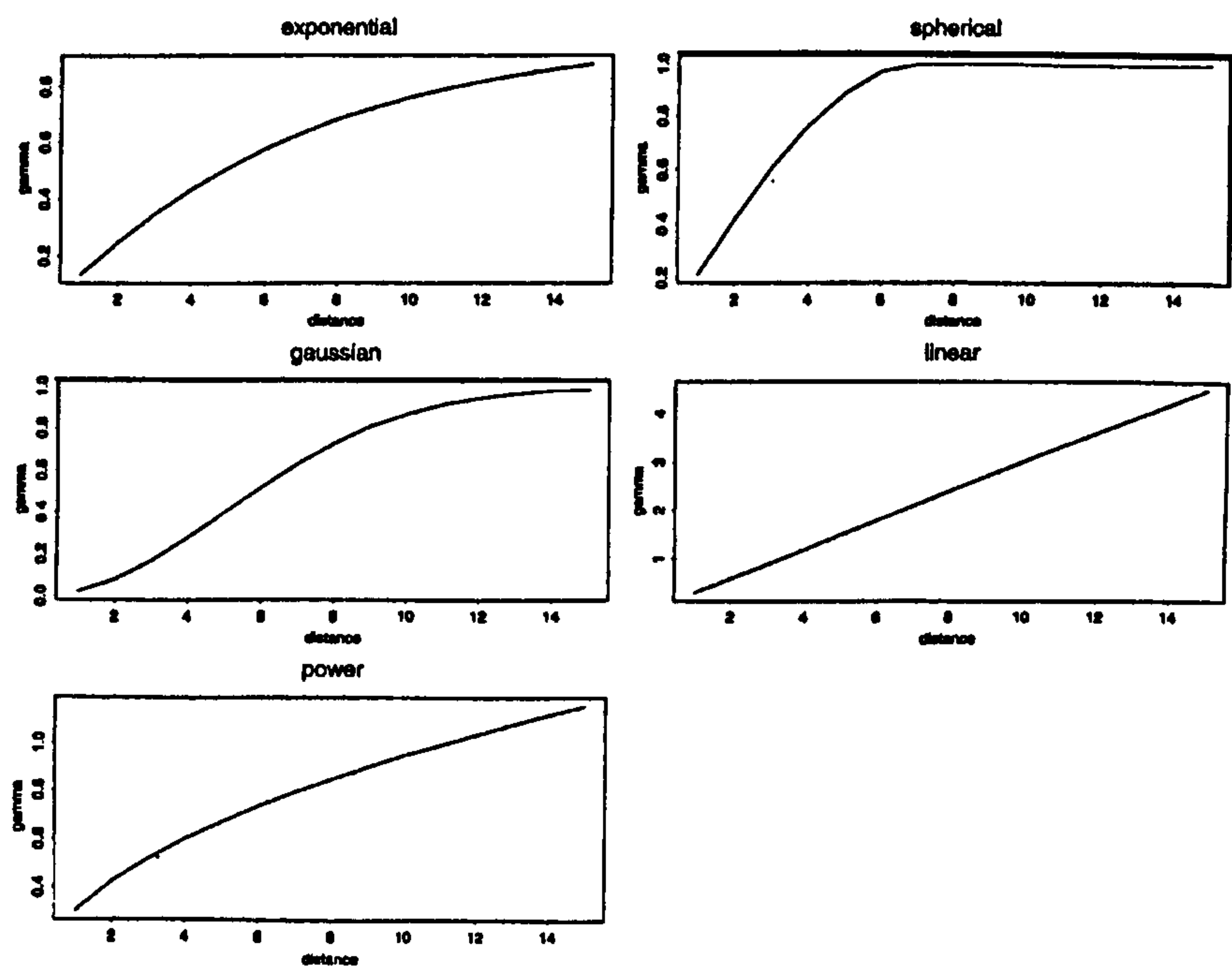


Figure A5.3 Main variogram models (Source: Kaluzny *et al.*, 1988)

Standardisation of data (mean=0, s.d.=1) enables variograms to be compared regardless of their absolute values (Boekhold and Van der Zee, 1992).

APPENDIX 6

SPATIAL INTERPOLATION: KRIGING

Introduction

Kriging is the estimation procedure used in geostatistics to determine unknown values using known values and their semi-variogram (Dorsel and La Breche, no date). It is a minimum-mean-squared-error method of spatial prediction that was developed empirically by the South African D.G. Krige in the 1950s and named kriging by Matheron in 1963 (Cressie, 1991). The technique uses weighted averages based on the location of data and the degree of spatial continuity present. Weights are determined so that the variance of estimation is minimised and the average error of estimation is zero (Spatial statistics, no date). Within soil science, kriging has generally been used for interpolation and mapping. A number of kriging types exist although ordinary or punctual kriging, as it is also known, is thought to be the best for estimating the amount of pollutant in a soil (Oliver and Webster, 1991). The theory and assumptions behind ordinary (punctual) kriging are described below.

Theory and assumptions

Punctual kriging is the simplest most common method of kriging that uses dimensionless points to estimate other dimensionless points (Dorsel and La Breche, no date). The technique assumes that the regionalized variable is stationary, although the local means do not necessarily have to be closely related to the population mean (Cressie, 1991). The technique estimates using only the samples in the local neighbourhood, usually the nearest 16 or 25 around the point estimated and therefore only the smaller lags of the variogram (Delcourt *et al.*, 1996). Values are estimated at the nodes of a fine grid, with contours or isarithms used to display variation (Oliver and Webster, 1991).

Having measured the value of a soil property (Z) at a number of points (n) within a particular region ($x_1, x_2, x_3, \dots, x_n$), Eq. 1 may be used to estimate the value of the same property at some unknown point (x_0), by the assigning of weights ($\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_n$) to each point (Figure A6.1). To avoid bias, the weights must be chosen to sum to 1 (Eq.2).

$$z(x_0) = \lambda_1 z(x_1) + \lambda_2 z(x_2) + \lambda_3 z(x_3) + \dots + \lambda_n z(x_n) \quad \text{Eq. 1}$$

$$1 = \lambda_1 + \lambda_2 + \lambda_3 + \dots + \lambda_n = \sum_{i=1}^n \lambda_i \quad \text{Eq. 2}$$

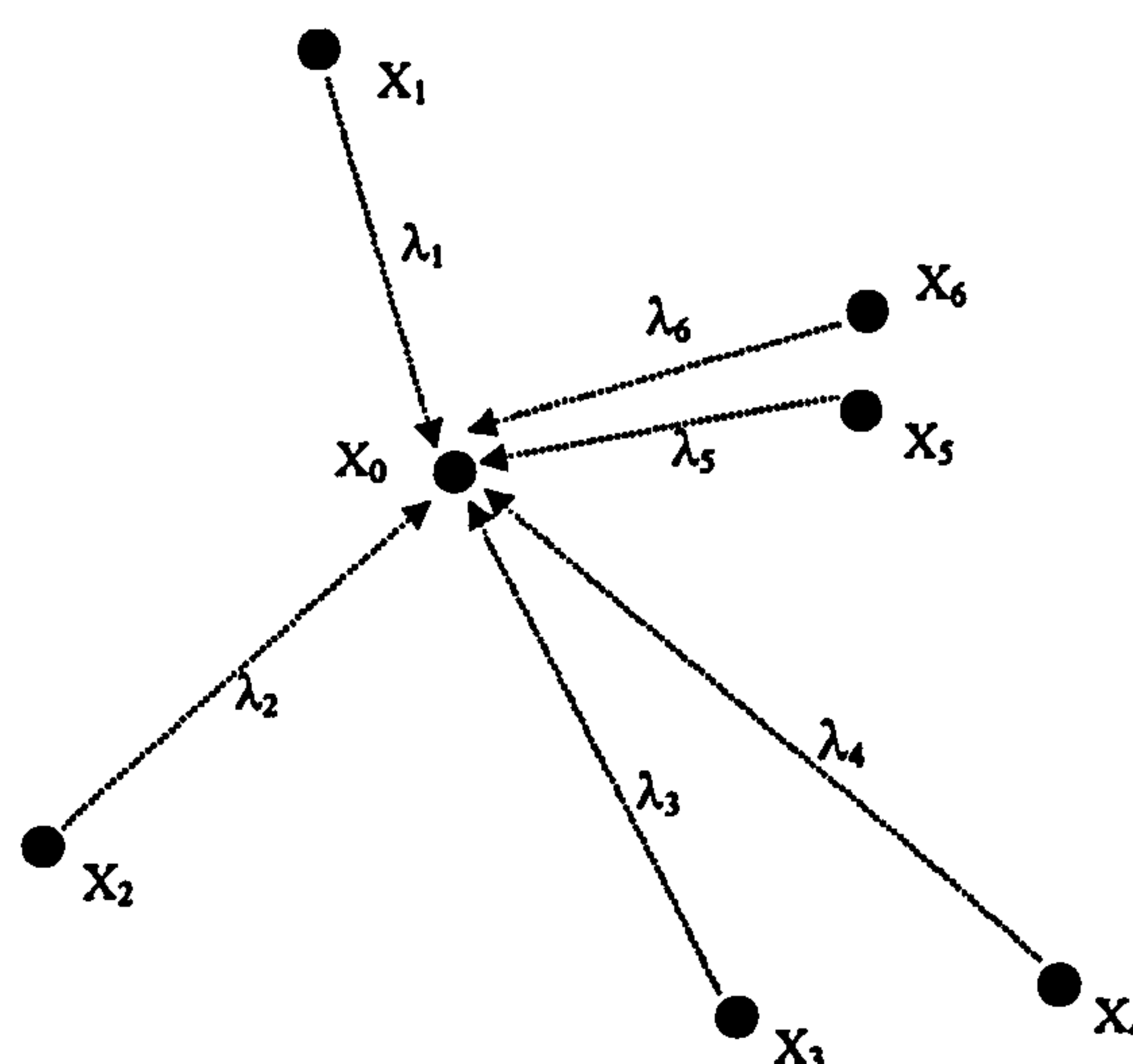


Figure A6.1 Plan of sampling points, showing kriging weights to estimate the value at point x_0

Kriging weights have three characteristics:

- points located closer to x_0 carry a larger weight than those located further away
 - points that occur in clusters carry less weight than lone points
 - a point may be down weighted if it is located beyond and screened by another point
- (Burgess and Webster, 1980; Oliver and Webster, 1991)

The weights are chosen to minimise estimation variances, producing as precise an estimate as possible, taking into account the spatial dependencies determined by the variogram, and the geometric relationships amongst observed points (Burgess and Webster, 1980). The estimation error is the difference between the estimated value and the actual value at a point. Assuming that the weights sum to one, the estimated value is said to be unbiased and the estimation variance, scatter of the estimates about the true value, may be calculated. Kriging attempts to choose weights to minimise estimation error (Dorsel and La Breche, no date).

The model for kriging may be defined by Eq.3, where $z(x)$ is the value of a property at point x within a certain neighbourhood (V). μ_v represents the mean value of the property within the neighbourhood and $\epsilon(x)$ a spatially dependent random component, the variation of which is defined by Eq.4 (Burgess and Webster, 1980).

$$z(x) = \mu_v + \epsilon(x) \quad \text{Eq. 3}$$

$$\text{var}[\epsilon(x) - \epsilon(x+h)] = E\{[\epsilon(x) - \epsilon(x+h)]^2\} = 2\gamma(h) \quad \text{Eq. 4}$$

If variation is isotropic (dependent only upon distance not direction) Eq. 4 equals $2\gamma(h)$. The mean must be constant over a neighbourhood, although may vary across the whole region. The variogram must remain constant across the region. The weights λ_i are calculated in the following manner. If the weights are to sum to 1, z_0 at point x_0 must be the same as the expectation $E[z(x_0)]$, making the estimator variance at x_0 the expected value of the squared difference between z_0 and $z(x_0)$ (Eq. 5) (Burgess and Webster, 1980).

$$E\{[z(x_0) - z_0]^2\} = -\sum_{i=1}^n \sum_{j=1}^n \lambda_i \lambda_j \gamma(x_i, x_j) + 2 \sum_{j=1}^n \lambda_j \gamma(x_0, x_j) \quad \text{Eq. 5}$$

$\gamma(x_i, x_j)$ is the value of the i -variogram along the line joining x_i and x_j at a distance $|x_j - x_i|$. In addition, the error variance must also be minimised with respect to each weight (λ_i), obtained by finding the partial derivatives with respect to each weight (λ_i). When Eq. 6 holds, the minimum variance is obtained (Burgess and Webster, 1980).

$$\sum_{j=1}^n \lambda_j \gamma(x_i, x_j) + \mu = \gamma(x_i, x_0) \quad \text{For } i = 1, 2, \dots, n \quad \text{Eq. 6}$$

The coefficients are given by Eq. 7

$$\begin{bmatrix} \lambda \\ \mu \end{bmatrix} = \mathbf{A}^{-1} \mathbf{b} \quad \text{Eq. 7}$$

Where,

$$\begin{bmatrix} \gamma(x_1, x_1) & \gamma(x_2, x_1) & \cdots & \gamma(x_n, x_1) & 1 \\ \gamma(x_1, x_2) & \gamma(x_2, x_2) & \cdots & \gamma(x_n, x_2) & 1 \\ \vdots & \vdots & & \vdots & \vdots \\ \gamma(x_1, x_n) & \gamma(x_2, x_n) & \cdots & \gamma(x_n, x_n) & 1 \\ 1 & 1 & \cdots & 1 & 0 \end{bmatrix} = \mathbf{A} \quad \text{Eq. 8}$$

$$\begin{bmatrix} \gamma(x_1, x_0) \\ \gamma(x_2, x_0) \\ \vdots \\ \gamma(x_n, x_0) \\ 1 \end{bmatrix} = \mathbf{b}, \text{ and } \begin{bmatrix} \lambda \\ \mu \end{bmatrix} = \begin{bmatrix} \lambda_1 \\ \lambda_2 \\ \vdots \\ \lambda_N \\ \mu \end{bmatrix} \quad \text{Eq. 9}$$

The minimum estimation variance is given by Eq. 10

$$\sigma_E^2 = \mathbf{b}^T \begin{bmatrix} \lambda \\ \mu \end{bmatrix} \quad \text{Eq. 10}$$

The vector of weights λ and the error of the estimate can therefore be obtained from the single matrix inversion of \mathbf{A} . As λ_i decreases with increasing distance between x_0 and x_i , the farthest points from x_0 can be omitted from the calculation (Burgess and Webster, 1980).

The accuracy with which kriged estimates are calculated depends upon the semi-variogram computed for the sampled points. Since only the nearest points are used, the variogram needs only to be accurate over the first few lags (Burgess and Webster, 1980). A nugget variance may have the effect of over estimating values at the sampling points whilst smoothing the surface between them, the strength of this effect depending upon the proportion of the nugget variance. The problem may be avoided either by not kriging at the sampling points or by choosing an interpolation grid the nodes of which do not coincide with any of the sampling points (Oliver and Webster, 1991)

APPENDIX 7

CORRELATION AND REGRESSION

Introduction

Correlation and regression are bivariate statistical analysis techniques, the main focus of which is to establish whether a relationship exists between two variables and describe the form of any relationship, respectively. Correlation analysis aims to identify the ideal relationship to which a given set of observations most closely approximates and measure the extent of the approximation (Walford, 1994). The most common form of correlation produces a numerical value or correlation coefficient, which measures both the strength and direction of any relationship. Regression analysis encapsulates the form of any relationship as an equation.

Pearson's product moment correlation

Pearson's product moment correlation coefficient based on the covariance, a bivariate measure of dispersion, was formulated in 1907 by Karl Pearson (Walford, 1994). The covariance (cv), defined as the average sum of the products of the deviation of two sets of data from their respective means (Gregory, 1978) is the mean deviation of a set of observations from their centroid, the central point within the observations (Eq. 1)

x and y represent the two variables, \bar{x} and \bar{y} the respective sample means and n the number of observations per sample.

$$cv = \frac{\sum (x - \bar{x})(y - \bar{y})}{n - 1} \quad \text{Eq. 1}$$

The covariance forms the numerator for the product moment correlation coefficient (r), the denominator being the product of the standard deviations of the two variables (Eq. 2).

$$r = \frac{\frac{1}{(n-1)} \sum (x - \bar{x})(y - \bar{y})}{\sqrt{\frac{1}{(n-1)} \sum (x - \bar{x})^2} \sqrt{\frac{1}{(n-1)} \sum (y - \bar{y})^2}} \quad \text{Eq. 2}$$

r varies between -1.0 to $+1.0$, the sign indicating the direction and the numerical value the strength of any relationship. A negative sign indicates a negative or indirect relationship, variable x increasing as variable y decreases, whilst a positive sign indicates a positive or direct relationship, variable x increasing as variable y increases. The closer the value is to 1.0 , the stronger the association between the two variables (Gregory, 1978; Webster and Oliver, 1990; Swan and Sandilands, 1995).

The significance of the r value may be determined using a table of critical values for Peasons 'r', that depend upon the sample size or degrees of freedom ($n-2$). The larger the sample size, the smaller r can be and yet still remain significant. Critical values are quoted for a number of significance levels, the most commonly used being the 95% level. If the r value is greater than or equal to the critical value at $n-2$ degrees of freedom, then the relationship / association between the two variables is statistically significant.

A correlation coefficient close to 1.0 does not indicate why a relationship exists between two variables, it purely indicates the degree of statistical association (Gregory, 1978). As the coefficient is determined in terms of the variance and standard deviations of the observed values, it assumes a normal frequency distribution. Transformation to normality is therefore a prerequisite for this test.

Linear regression

Regression analysis or analysis of causation determines the nature of control one variable, the independent variable, has over another, the dependent variable (Walford, 1994). Hence, for any value of the independent variable (X) the corresponding value of the dependent variable (Y) may be determined either graphically or mathematically.

In the case of perfect correlation ($r=1.0$), a straight line could be drawn exactly through the distribution of two sets of data observations when plotted on a scatter graph (Figure A7.1a). Perfect correlation is however rarely found, instead when graphed the points display a degree of scatter (Figure A7.1b) (Gregory, 1978). In this case a line may be drawn to summarise the relationship, from which the most likely value of the dependent variable may be determined when that of the index variable is known. This line is known as the regression line and is orientated so that the sum of the squares of the

deviations between the actual points and the line is a minimum (the method of least squares) (Figure A7.2). The regression line equation is determined using the correlation coefficient (r), and the mean (\bar{x} and \bar{y}) and standard deviation (σ_x and σ_y) of both data sets (Eq. 3). Where y is the dependent and x the independent variable (Gregory, 1978).

$$y - \bar{y} = r \frac{\sigma_y}{\sigma_x} (x - \bar{x})$$

Eq. 3

The equation for the regression line will be of the form shown in Eq. 4, where m represents the gradient of the line and c the intercept on the y axes. This equation represents the general form of the relationship between the two data sets.

$$y = mx + c$$

Eq. 4

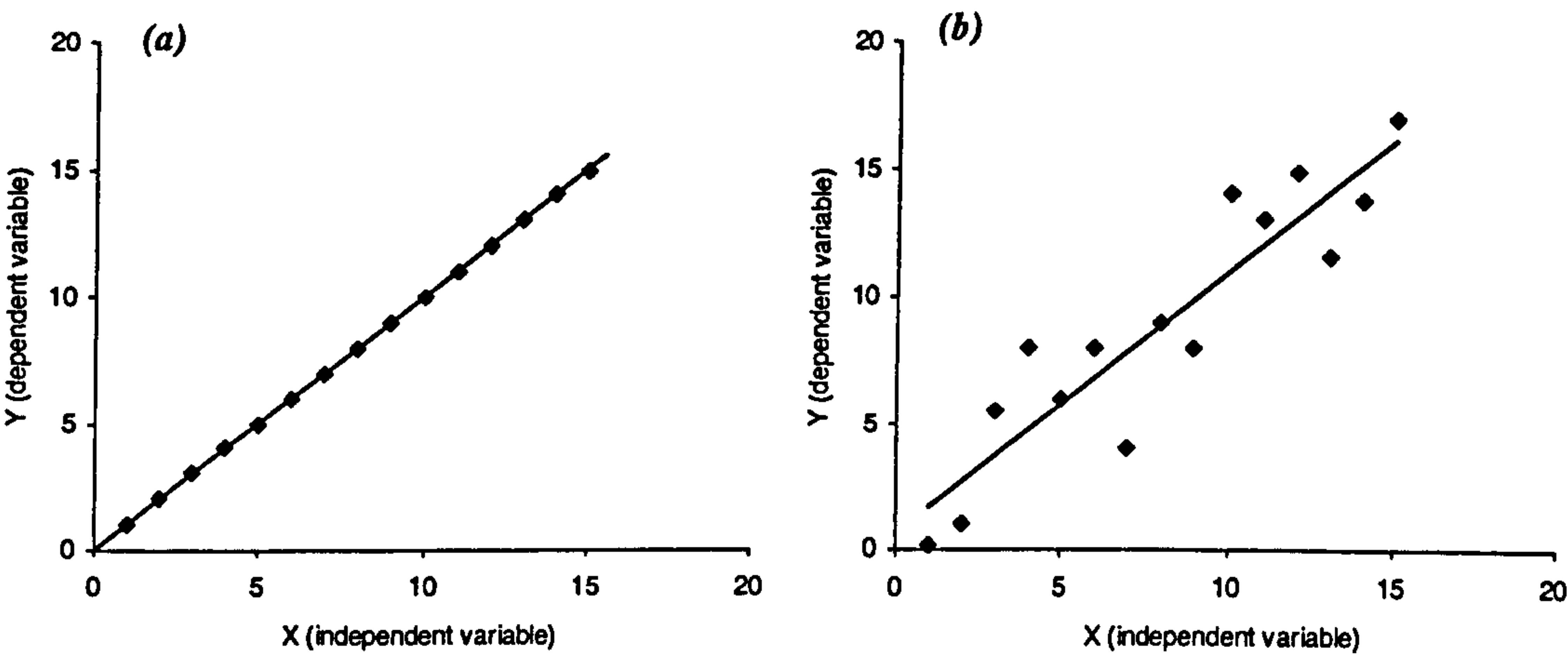


Figure A7.1 Regression lines. (a) $r = 1.0$; (b) $r < 1.0$

The coefficient of determination, r^2 , indicates the level of explanation in the relationship, i.e. the degree to which the variation in Y is explained by variation in X . The analysis assumes that both data sets are normally distributed, that interval scale data are being used and that any errors in the measurement of X are small in relation to errors in the measurement of Y . Data may be transformed as necessary (King, 1969; Walford, 1994).

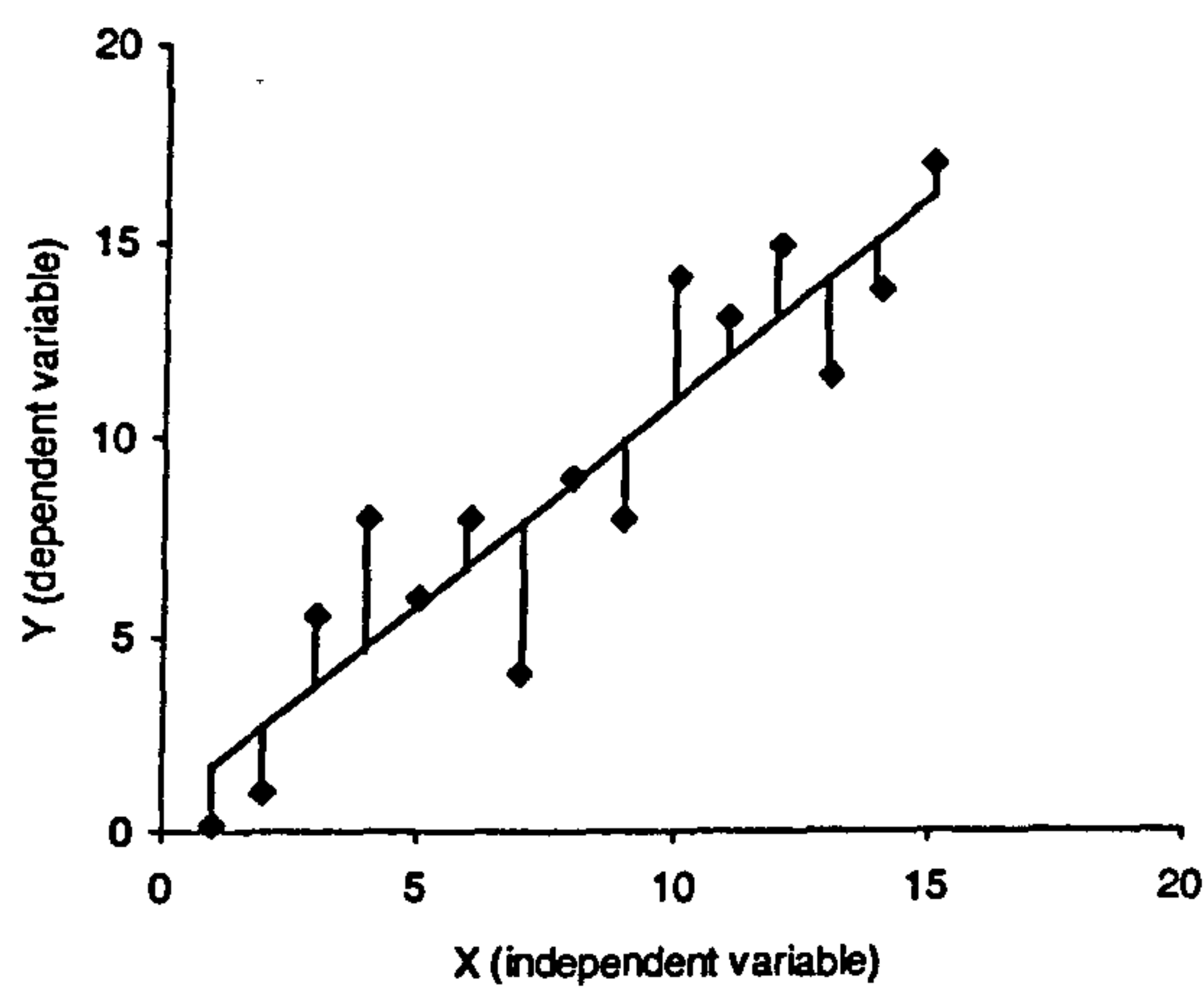


Figure A7.2 Regression line fitting, method of least squares

APPENDIX 8

PRINCIPAL COMPONENTS ANALYSIS (PCA)

Introduction

Multivariate analysis techniques allow the simultaneous analysis of any number of variables (Swan and Sandilands, 1995), which due to the complexity of most geographical problems, examining numerous interrelated variables, are favoured in geographical analysis (King, 1969). Numerous techniques exist of which principal component analysis is most suited to showing relationships between soil properties (Oliver and Webster, 1991). Essentially, PCA determines the directions of maximum variance within the data, using these to ordinate data in a number of dimensions and interpreting them as factors influencing the data.

Theory and assumptions

Principal components analysis involves the transformation of a set of variables ($x_1, x_2, \dots x_n$) into a new set of uncorrelated variables ($y_1, y_2, \dots y_n$), that exactly preserve the total variance associated with the original variables. The technique derives as many components, known as principal components, as there are variables, whereby y_1 accounts for the highest proportion of the total variance, y_2 the second highest etc. (King, 1969). In general the majority of the variance may be accounted for by comparatively few of the new variables.

A bivariate normal distribution of two correlated variables, X_1 and X_2 , may be represented by Figure A8.1, where μ_1 and μ_2 represent the means of the two distributions and Y_1 and Y_2 the principal axes. The variation accounted for by Y_1 is far greater than that accounted for by X_1 or X_2 , the original axes, hence the data could be represented in one dimension by projecting the data points orthogonally onto Y_1 , the principal axes, forgoing the remainder of the variation (King, 1969). This is the basis of principal components analysis (Webster, 1977). Information need not be lost when dealing with only two variables. The principal may be extended to several dimensions, representing numerous variables as a two-dimensional scatter graph or three-dimensional model.

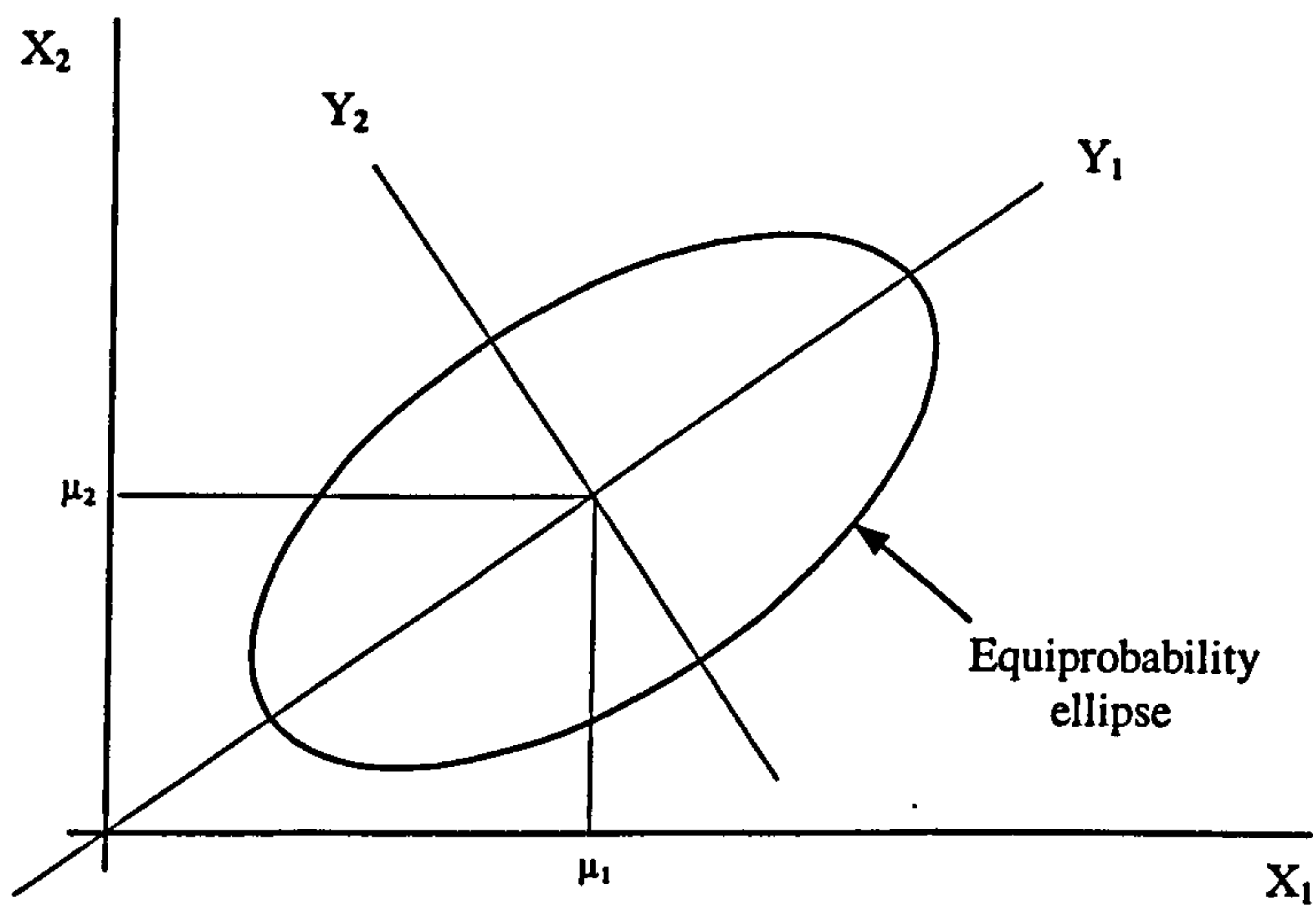


Figure A8.1 Representation of a bivariate normal distribution of two correlated variables.

Variances of the original variables must be approximately equal or the direction of the principal axes will be controlled by those variables with the largest variances (Webster, 1977). Variables measured on different scales must be standardised, although it is not essential that variables are normally distributed (King, 1969).

Consider point P located at position x_1, x_2 on the axes OX_1 and OX_2 , where θ represents the angle that the principal axes makes with the original axes (Figure A8.2). Point P is represented on the principal axes, Y_1 and Y_2 by the co-ordinates y_1 and y_2 that may be determined by geometry (Eq. 1) (Webster, 1977).

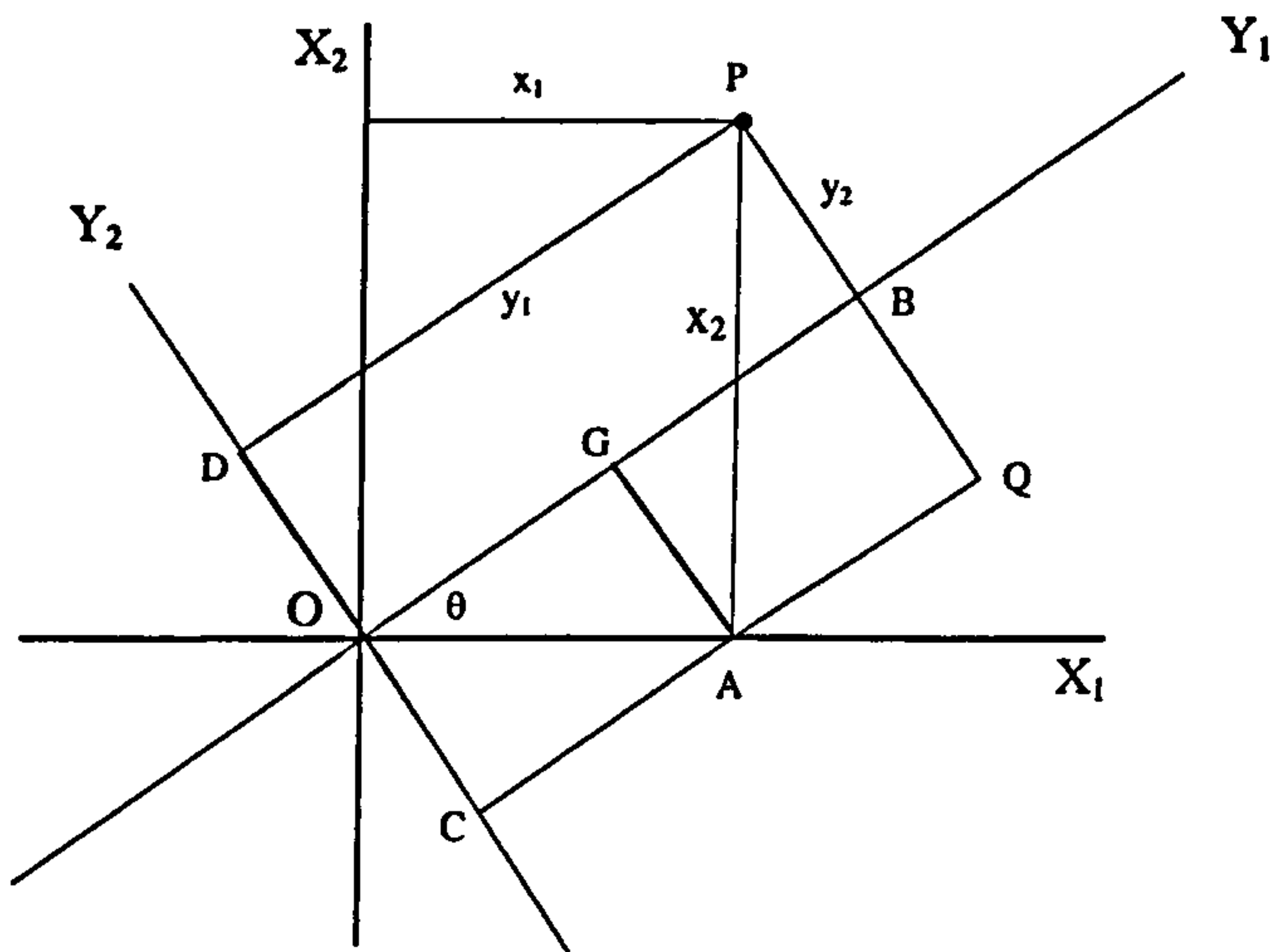


Figure A8.2 The geometry of axis rotation (Adapted from Webster, 1977)

$$\left. \begin{aligned} y_1 &= OB = x_1 \cos \theta + x_2 \sin \theta \\ y_2 &= OD = -x_1 \sin \theta + x_2 \cos \theta \end{aligned} \right\} \quad \text{Eq. 1}$$

The two equations constitute a linear transformation of form

$$\mathbf{y} = \mathbf{x}\mathbf{C}' \quad \text{Eq. 2}$$

Where

$$\mathbf{C} = \begin{bmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{bmatrix} = \begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix} \quad \text{Eq. 3}$$

Note that

$$\begin{aligned} \mathbf{C}\mathbf{C}' &= \begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix} \begin{bmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{bmatrix} \\ &= \begin{bmatrix} \cos^2 \theta + \sin^2 \theta & -\cos \theta \sin \theta + \sin \theta \cos \theta \\ -\sin \theta \cos \theta + \cos \theta \sin \theta & \cos^2 \theta + \sin^2 \theta \end{bmatrix} \\ &= \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} = \mathbf{I} \end{aligned} \quad \text{Eq. 4}$$

If θ , the angle between the original and principal axes is determined, the co-ordinates $y_1 y_2$ of any point $x_1 x_2$ may be determined. The new variables y_1 and y_2 will be uncorrelated hence their variance-covariance matrix will exhibit a covariance of 0. Representing the variances of the principal axes by λ_1 and λ_2 the variance-covariance matrix is of the form (Eq. 5) (see Eq. 3) (Webster, 1977).

$$\frac{1}{n-1} \mathbf{Y}'\mathbf{Y} = \begin{bmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{bmatrix} = \mathbf{\Lambda} = \frac{1}{n-1} \mathbf{C}\mathbf{X}'\mathbf{X}\mathbf{C}' \quad \text{Eq. 5}$$

As $\frac{1}{n-1} \mathbf{XX}' = \mathbf{A}$, Λ the variance-covariance matrix may be written, $\Lambda = \mathbf{CAC}'$. Post-multiplying by \mathbf{C} , we have $\Lambda\mathbf{C} = \mathbf{CA}$ which when multiplied out gives (Webster, 1977),

$$\begin{bmatrix} c_{11}\lambda_1 & c_{12}\lambda_1 \\ c_{21}\lambda_2 & c_{22}\lambda_2 \end{bmatrix} = \begin{bmatrix} c_{11}a_{11} + c_{12}a_{21} & c_{11}a_{12} + c_{12}a_{22} \\ c_{21}a_{11} + c_{22}a_{12} & c_{21}a_{12} + c_{22}a_{22} \end{bmatrix} \quad \text{Eq. 6}$$

$$\begin{bmatrix} c_{11}(a_{11} - \lambda_1) + c_{12}a_{21} & c_{11}a_{12} + c_{12}(a_{22} - \lambda_1) \\ c_{21}(a_{11} - \lambda_2) + c_{22}a_{12} & c_{21}a_{12} + c_{22}(a_{22} - \lambda_2) \end{bmatrix} = \mathbf{0}$$

$\mathbf{0}$ being a 2 x 2 matrix with all elements 0.

Two pairs of simultaneous equations may be equated from Eq. 6, taken from the first and second rows respectively (Webster, 1977).

$$\begin{aligned} c_{11}(a_{11} - \lambda_1) + c_{12}a_{21} &= 0 \\ c_{11}a_{12} + c_{12}(a_{22} - \lambda_1) &= 0 \end{aligned} \quad \text{Eq. 7}$$

and

$$\begin{aligned} c_{21}(a_{11} - \lambda_2) + c_{22}a_{12} &= 0 \\ c_{21}a_{12} + c_{22}(a_{22} - \lambda_2) &= 0 \end{aligned} \quad \text{Eq. 8}$$

$c_{11} = 0$ and $c_{12} = 0$ is one solution to these equations, although, this is not possible as y_1 would also be zero. The determinant must equal zero if the equations are to have another solution, hence in general (Webster, 1977),

$$\begin{vmatrix} a_{11} - \lambda & a_{21} \\ a_{12} & a_{22} - \lambda \end{vmatrix} = 0 \quad \text{Eq. 9}$$

When multiplied out, the determinant gives the quadratic equation in Eq. 10. The roots (λ_1 and λ_2) of which are found by solving determinantal equation (Eq. 11).

$$\lambda^2 - (a_{11} + a_{22})\lambda + a_{11}a_{22} - a_{12}a_{21} = 0 \quad \text{Eq. 10}$$

$$|\mathbf{A} - \lambda \mathbf{I}| = 0 \quad \text{Eq. 11}$$

The roots are known as latent roots, characteristic roots or eigenvalues and the associated vectors c_1 and c_2 the latent vectors or eigenvectors. As the quadratic is of the form $x^2 - bx + q = 0$, b is the sum of the roots and q the product (Webster, 1977). We may solve for c by recalling the earlier simultaneous equations, which on re-arranging give

$$c_{12} = \frac{(a_{11} - \lambda_1)}{a_{21}} c_{11} \quad \text{Eq. 12}$$

As $c_{11}^2 + c_{12}^2 = 1$, c_{11} and c_{12} can be determined.

When the elements of \mathbf{C} have been determined, the co-ordinates of any point may be calculated given its value on the original axes (Webster, 1977).

APPENDIX 9

NON-HIERARCHICAL CLUSTER ANALYSIS

Introduction

Non-hierarchical classification or dynamic clustering has often been over looked in preference to hierarchical methods, for the classification of multivariate data. However, when data appear to lack any spatial structure non-hierarchical methods are likely to be more appropriate, discriminating more accurately between groups of samples. The technique sub-divides a set of samples about which, various parameters are known, into a number of clusters or groups. Clusters are identified so as to maximise the differences between the groups whilst creating clusters of minimum within group variation. An optimal sub-division of the data is therefore produced (Webster and Oliver, 1990). The technique is an iterative process, utilising a test criterion to assess each classification following movement of individual samples between groups.

Theory and assumptions

Three main test criteria have been developed to assess the efficiency of non-hierarchical clustering, the choice of which depends on the nature of the problem and form of the data. The main test criteria are listed below and maybe split into two groups, those that measure dispersion within groups and those which measure separation between groups (Table A9.1).

criterion	measure		appropriateness
SS_w	dispersion within groups, measuring compactness	sum of squares of deviations from the group means. original data must be standardised	clustering known to be weak
Wilks's (L)	dispersion within groups, measuring average compactness of the groups	$ W / T $ <i>compact groups = small L</i>	presence of elongated clusters
Trace $W^{-1}B$	separation between group centroids	sum of weighted (by group size) mahalanobis D^2 between the whole data set and centroids of the clusters. an unweighted sum is known as $Tr W^{-1}B$ <i>compact groups > Mahalanobis distances between them</i>	

Table A9.1 Main test criteria used in non-hierarchical cluster analysis

The general equation of multivariate analysis of dispersion (Eq 1) is used to derive the test criteria, where \mathbf{T} = the total sums of squares and products (SSP) matrix, \mathbf{W} = SSP matrix within groups and \mathbf{B} = SSP matrix between-groups. The test criteria for the optimisation of classification are functions of \mathbf{W} and \mathbf{B} (Table A9.1).

$$\mathbf{T} = \mathbf{W} + \mathbf{B} \quad \text{Eq 1}$$

Initial clusters

A number of methods have been devised to sub-divide the data into initial clusters from which the data is re-allocated, on the basis of the test criterion, to improve classification. These include:

- The cutting of a dendrogram, produced via a hierarchical clustering technique .
- Intuitive judgement or use of previous knowledge regarding clustering of the data.
- Random partitioning, such as the sub-division of data into a number of evenly sized groups according to the order of the data (i.e. g data points are divided into k groups of m , group k_1 consisting of the first m data points in the set, k_2 the second m and k_n the final m data points).

A number of other methods also exist (Webster and Oliver, 1990).

Reallocation

Following initial allocation of the samples to clusters, the chosen test criterion is calculated. Individual samples are then moved between groups with the test criterion re-calculated following each move. A move is retained if it leads to an improvement of the test criterion, however if not, the sample is returned to its previous cluster. The process is repeated iteratively until no further improvements can be made to the criterion. The resultant classification represents a local rather than a global optimum, as despite none of the moves improving the classification there maybe a better classification, if only it could be found. A locally optimised classification is often achieved for poorly clustered data. It is possible however to force further moves in the form of between group exchanges once a local optimum has been achieved. An algorithm for this is included within Genstat. Again, test criteria are calculated following each exchange with exchanges continuing until no further improvement in the test criteria is achieved.

Optimum number of clusters

In theory, the above techniques can be used to sub-divide the data into any number of clusters however, if data are at all clustered then an optimum number of groups will exist. If this optimum is not known, Wilks's criterion, L , may be used as a measure of goodness to identify the optimum number of classes within a data set. If L is calculated for different numbers of groups, $g = 2, 3, 4, \dots, n$, a plot of g^2L vs. g will decline steadily from a $g^2L = 1$ at $g = 1$, for a homogenous population. However, in a heterogeneous population a change in slope will occur, corresponding with the optimum number of clusters present within the data (Figure A9.1).

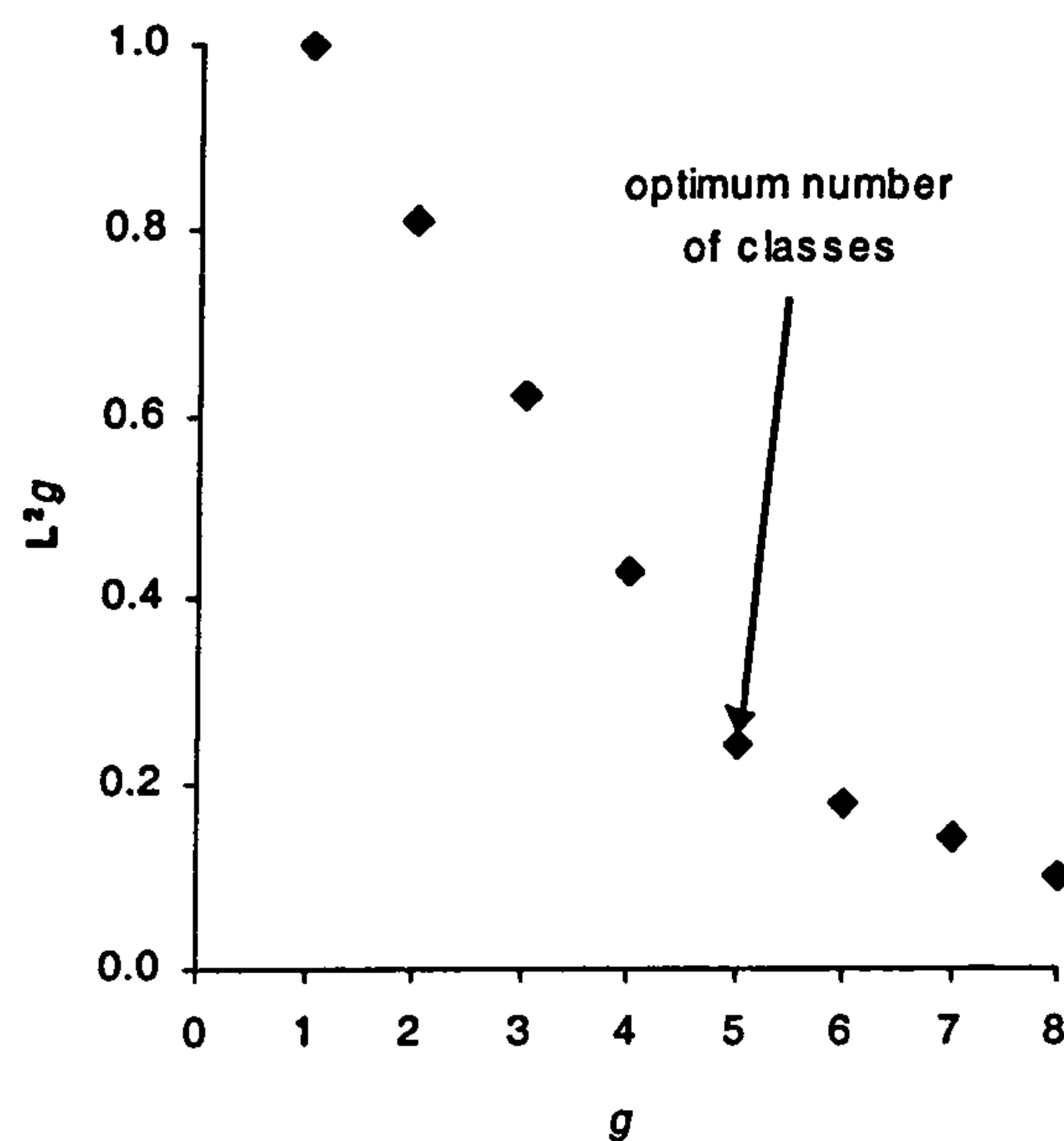


Figure A9.1 Graph of L^2g vs g , indicating optimum number of classes

APPENDIX 10

RAW DATA

sample no.	total Pb (mg/kg)	total Zn (mg/kg)
1	369	62
2	296	69
3	252	75
4	180	712
5	366	142
6	447	238
7	221	79
8	215	93
9	565	83
10	584	91
11	283	84
12	270	72
13	386	65
14	378	107
15	130	79
16	217	95
17	398	76
18	291	62
19	732	121
20	327	68
21	310	102
22	303	87
23	816	146
24	205	125
25	370	87
26	260	74
27	322	90
28	269	163
29	177	112
30	229	128
31	692	93
32	783	115

Table A9.1 Raw data Town Moor site.

sample no.	total Pb (mg/kg)	total Zn (mg/kg)
1	237	159
2	163	139
3	2038	59
4	2838	74
5	211	73
6	270	83
7	1860	93
8	1182	82
9	223	93
10	349	61
11	451	68
12	404	63
13	1121	82
14	850	78
15	729	114
16	283	112
17	392	65
18	290	59
19	109	62
20	93	54
21	100	48

Table A9.2 Raw data Nuns Moor site.

sample no.	total Pb (mg/kg)	total Zn (mg/kg)
1	214	163
2	119	145
3	136	142
4	79	50
5	60	49
6	82	74
7	65	49
8	59	38
9	68	46
10	45	48
11	43	50
12	75	49
13	68	54
14	56	55
15	67	43
16	126	49
17	279	31
18	60	43
19	92	42
20	67	20
21	79	49
22	129	53
23	81	35
24	31	50
25	104	128
26	185	282
27	237	220
1w	123	114
2w	98	54
3w	66	77
4w	92	62
5w	83	69
6w	119	97
7w	77	76
8w	91	78
9w	107	59
10w	136	198
11w	94	260
12w	83	66
13w	83	75
15w	142	78
16w	95	71
17w	108	100
18w	130	119
19w	195	145
20w	86	68
21w	558	1082
22w	100	91
23w	74	96

Table A9.3 Raw data Hazelrigg site (w – wooded area).

APPENDIX 4

TECHNICAL ASPECTS OF THE INSTRUMENTATION AND OPERATION OF AAS

The principle of atomic absorption spectrometry

The measurement of absorption of electromagnetic radiation, visible and UV, passed through an atomic vapour, resulting in changes in electronic structure of the atoms from ground state to higher electronic levels (Haswell, 1991; Skoog and Leary, 1992;).

Theory

Absorbance, A , of the electromagnetic radiation is the logarithm of the ratio of the incident, P_i , to transmitted, P_t , power of the light (Eq. 1).

$$A = \log_{10} \left[\frac{P_i}{P_t} \right] \quad \text{Eq. 1}$$

The extent to which radiation, of a given frequency, is absorbed is related to the path length, L , in the absorbing medium and the concentration of atoms within the vapour (Eq. 2, Figure A4.1). k is the absorption coefficient, a function of several properties, including the concentration of atoms which can absorb radiation at the given frequency and wavelength of the radiation.

$$P_i = P_t e^{kL} \quad \text{Eq. 2}$$

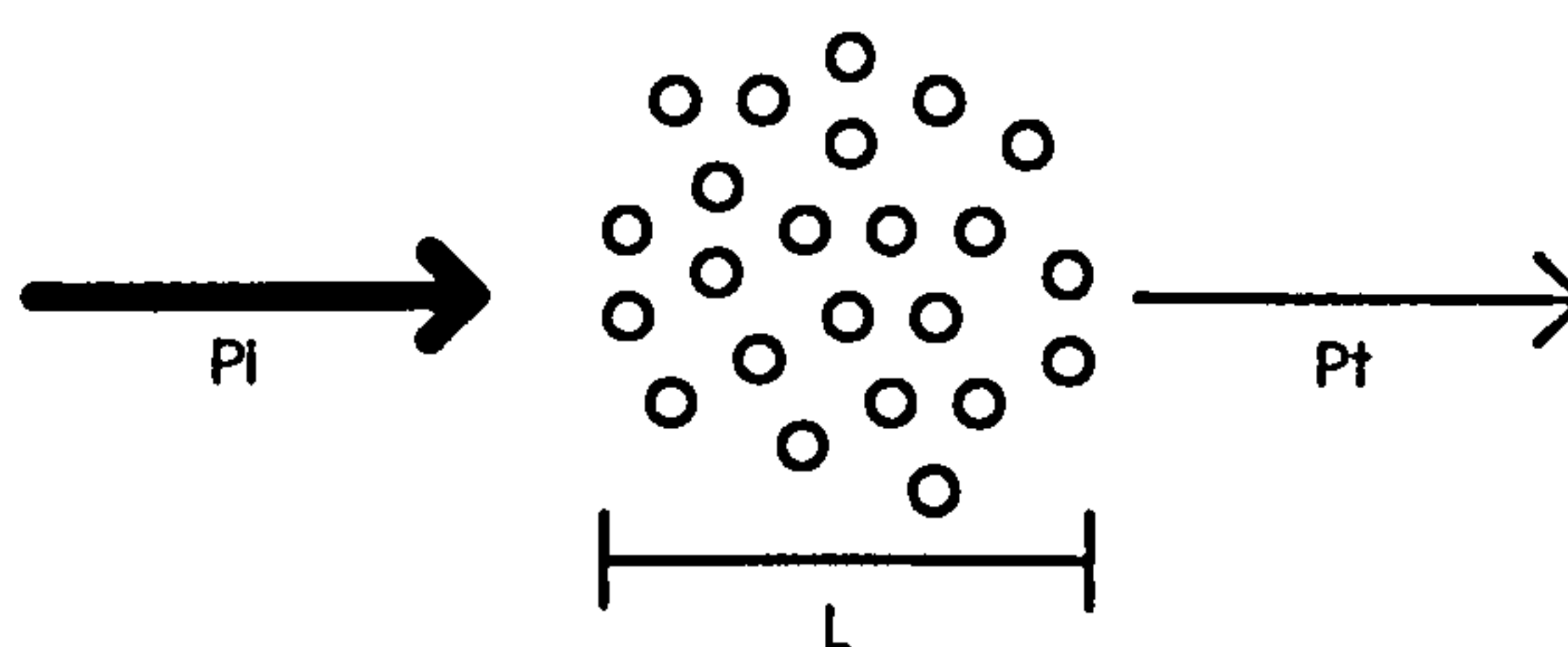


Figure A4.1 The absorption of a light beam passing through a distance, L , of an atomic vapour.

sample no.	total Pb (mg/kg)	total Zn (mg/kg)
1	282	173
2	268	177
3	206	151
4	302	429
5	250	205
6	308	169
7	206	185
8	190	127
9	172	112
10	140	109
11	234	118
12	210	128
13	184	110
14	314	199
15	5598	1328
16	426	226
17	276	158
18	392	246
19	242	126
20	204	129
21	468	247
22	220	135
23	208	116
24	198	117
25	240	111
26	154	150
27	340	227
28	182	132
29	174	120
30	266	235
31	190	87
32	202	125
33	298	153
34	178	126
35	168	122

Table A9.4 Raw data South Gosforth site.

sample no.	total Pb (mg/kg)	total Zn (mg/kg)	pH	organic matter (%)	CEC (me/100g)
1	265	127	5.7	28.4	29.7
2	547	73	6.3	17.2	24.7
3	4566	70	4.5	35.2	30.5
4	3371	63	4.5	26.4	29.5
5	380	62	4.7	37.0	37.8
6	1993	89	4.7	45.4	27.0
7	4503	90	4.9	31.7	34.9
8	764	89	5.4	28.7	36.1
9	1357	67	4.4	34.5	32.8
10	775	80	5.4	23.1	28.9
11	2286	88	5.1	39.6	38.3
12	227	77	4.4	22.8	39.9
13	1216	71	4.9	31.9	34.5
14	2153	86	4.6	35.4	32.3
15	2407	185	4.2	30.4	31.6
16	1843	46	4.5	24.5	16.3
17	353	85	6.3	21.7	25.1
18	107	149	6.1	14.0	18.8
19	899	103	4.9	31.4	28.5
20	351	65	4.8	24.0	26.4
21	3400	81	4.6	31.8	24.4
22	502	77	4.7	25.2	24.4
23	535	78	4.7	37.3	21.6
24	455	72	4.8	30.0	25.9
25	337	80	5.3	28.2	32.9
26	732	72	5.9	22.3	29.3
27	402	78	5.8	17.0	22.6
28	2476	75	4.1	38.5	19.4
29	906	62	4.9	27.5	27.0
30	537	68	4.1	29.9	30.4
31	5631	174	4.4	38.0	32.3
32	665	65	4.3	31.6	33.9
33	1972	86	4.4	34.9	37.8
34	1273	83	4.4	40.4	37.0
35	648	75	5.4	19.8	29.7
36	1991	86	4.7	23.7	29.0
37	450	82	4.4	26.3	28.8
38	840	78	4.0	20.4	26.6
39	605	66	4.1	26.4	29.0
40	1931	74	4.3	25.4	28.8
41	3449	80	4.9	35.6	40.2
42	2793	65	4.7	18.6	25.9
43	667	74	5.3	25.1	31.3
44	1735	56	4.9	20.8	23.6
45	205	91	4.8	25.5	26.6
46	1152	61	4.6	20.5	26.3
47	629	56	5.0	22.8	24.0
48	830	66	5.1	15.3	18.9
49	1078	46	4.4	14.7	11.8
50	2220	61	4.5	23.5	27.7
51	3560	50	4.7	23.7	31.2
52	2364	51	4.5	20.5	24.5
53	1988	58	4.7	21.3	26.4
54	554	58	4.6	13.8	18.8
55	2023	48	4.7	18.7	25.8
56	1540	48	4.7	20.6	28.0
57	280	66	4.9	16.0	20.9
58	1131	46	4.8	19.6	25.6
59	291	62	5.7	19.2	27.0
60	4052	60	4.5	24.0	29.0
61	1411	53	4.1	27.9	25.1
62	621	62	4.6	15.9	20.0
63	540	72	4.7	15.5	24.4

Table A9.5 Raw data plot I, top soil.

sample no.	TPb-exc (mg/kg)	TPb-red (mg/kg)	TPb-oxi (mg/kg)	TPb-res (mg/kg)
1	7	63	133	26
2	8	203	233	66
3	249	1923	2029	334
4	369	1157	1200	189
5	13	122	256	23
6	73	684	1027	130
7	303	1593	1553	156
8	40	197	375	39
9	98	369	423	74
10	29	302	419	51
11	112	734	1384	184
12	17	89	115	29
13	62	246	672	68
14	92	570	887	96
15	172	928	944	109
16	186	784	684	89
17	12	126	202	47
18	3	34	45	50
19	30	313	464	117
20	23	119	141	21
21	262	1602	1288	357
22	23	197	223	68
23	17	148	286	52
24	15	148	211	95
25	10	97	202	52
26	32	308	370	72
27	14	146	171	51
28	199	1034	996	244
29	50	424	431	83
30	28	192	241	57
31	298	1962	1931	783
32	35	254	324	106
33	115	660	1058	182
34	50	459	725	93
35	17	243	337	81
36	112	837	1015	187
37	24	166	234	64
38	60	322	364	100
39	48	242	310	56
40	103	766	963	184
41	134	1089	1544	381
42	295	1233	1047	211
43	24	224	366	64
44	121	786	799	121
45	7	65	119	33
46	92	503	588	114
47	37	246	325	58
48	57	377	405	95
49	186	489	335	83
50	201	880	930	166
51	284	1501	1802	255
52	226	932	1068	167
53	234	743	749	167
54	58	218	218	71
55	241	690	845	191
56	182	469	644	134
57	16	98	117	49
58	124	513	506	116
59	6	81	132	53
60	491	1569	2028	381
61	131	613	659	128
62	74	287	243	80
63	38	233	235	74

Table A9.6 Raw data (Pb fractionation) plot I, top soil.

sample no.	TZn-exc (mg/kg)	TZn-red (mg/kg)	TZn-oxi (mg/kg)	TZn-res (mg/kg)
1	12	10	29	65
2	9	5	16	51
3	9	4	18	44
4	12	1	16	43
5	18	7	21	34
6	25	11	20	39
7	19	5	16	50
8	26	6	21	42
9	15	1	21	46
10	11	7	22	51
11	17	11	18	45
12	19	8	19	40
13	14	4	20	35
14	14	6	18	36
15	13	5	19	37
16	7	2	13	26
17	7	5	13	92
18	20	12	16	53
19	23	12	13	50
20	14	6	9	42
21	24	8	7	43
22	19	11	9	38
23	20	10	9	30
24	15	7	9	37
25	16	10	9	38
26	10	6	7	47
27	8	5	7	51
28	15	4	9	50
29	12	6	7	38
30	17	8	9	31
31	22	11	19	96
32	12	6	7	38
33	15	16	9	47
34	21	14	9	36
35	7	7	10	50
36	18	8	7	52
37	20	10	8	44
38	16	5	9	51
39	12	4	6	37
40	15	9	6	45
41	16	12	8	40
42	10	4	4	47
43	10	6	7	42
44	9	7	4	43
45	21	7	11	48
46	9	4	5	44
47	7	4	6	37
48	4	4	10	50
49	5	1	6	38
50	16	3	6	39
51	4	3	11	32
52	4	3	12	30
53	7	4	13	35
54	3	7	12	34
55	3	3	11	31
56	2	2	11	28
57	7	3	5	43
58	4	1	4	31
59	5	5	15	38
60	8	3	4	37
61	10	3	5	32
62	10	3	4	46
63	9	3	4	46

Table A9.7 Raw data (Zn fractionation) plot I, top soil.

sample no.	total Pb (mg/kg)	total Zn (mg/kg)	pH	organic matter (%)	CEC (me/100g)
1	245	132	4.7	15.8	22.2
2	386	73	6.4	13.2	21.1
3	679	56	4.4	15.1	20.0
4	840	54	4.3	16.1	17.6
5	394	57	4.5	4.9	19.6
6	407	54	4.2	15.2	22.5
7	1406	71	4.4	15.0	22.4
8	654	75	4.5	14.4	25.0
9	367	58	4.2	15.5	19.7
10	486	72	4.9	13.6	21.0
11	559	56	4.6	13.8	15.4
12	277	71	4.7	13.3	17.6
13	581	54	4.6	14.9	17.5
14	600	61	4.7	16.9	18.3
15	663	58	4.2	15.6	18.3
16	396	43	4.3	13.4	17.6
17	229	86	5.8	13.9	13.4
18	112	155	6.3	3.8	11.6
19	383	58	4.5	14.1	15.3
20	282	58	4.6	13.8	12.7
21	890	67	4.2	13.4	15.7
22	141	54	4.4	11.3	15.3
23	285	51	4.4	12.9	10.0
24	499	49	3.9	15.0	13.5
25	384	68	4.6	12.6	19.2
26	708	72	4.8	12.3	18.4
27	408	74	5.0	12.1	15.8
28	695	52	3.8	13.4	15.4
29	1020	56	4.4	16.6	19.8
30	583	59	4.1	16.8	34.1
31	1995	75	4.3	14.6	34.4
32	628	47	4.1	17.6	32.1
33	2031	57	4.1	16.6	18.0
34	912	46	4.1	18.1	24.2
35	402	57	5.4	14.1	25.1
36	637	58	4.6	12.5	21.0
37	765	58	4.3	14.6	22.3
38	228	56	4.3	11.6	19.4
39	593	60	4.1	15.2	21.4
40	824	47	4.0	13.1	16.9
41	812	54	4.2	14.5	12.5
42	368	50	4.0	9.2	12.1
43	335	52	4.0	12.4	12.9
44	184	49	3.9	10.3	15.3
45	221	70	4.0	11.8	12.8
46	207	62	4.6	10.3	17.3
47	314	51	4.5	13.7	15.7
48	244	64	5.0	10.2	14.9
49	1504	48	4.2	15.8	14.8
50	259	54	4.6	10.0	10.8
51	2384	53	4.4	16.2	17.0
52	199	51	4.7	9.4	9.6
53	1295	64	4.3	14.5	14.3
54	213	60	4.3	8.6	14.0
55	1644	50	4.3	14.6	17.3
56	162	53	4.6	8.7	11.4
57	231	56	4.6	14.3	14.2
58	358	72	4.8	9.3	13.4
59	304	66	5.2	14.9	14.9
60	311	46	4.5	9.2	11.6
61	586	49	4.1	14.5	12.4
62	85	51	4.8	9.1	11.9
63	646	59	4.5	15.6	16.2

Table A9.8 Raw data plot I, sub soil.

sample no.	SPb-exc (mg/kg)	SPb-red (mg/kg)	SPb-oxi (mg/kg)	SPb-res (mg/kg)
1	9	57	111	62
2	7	135	141	78
3	127	302	223	54
4	144	378	278	64
5	43	133	116	15
6	42	141	151	46
7	208	712	510	87
8	54	231	230	63
9	40	152	154	37
10	41	191	186	48
11	71	196	164	37
12	15	90	111	43
13	57	196	192	40
14	64	237	224	50
15	97	275	213	43
16	68	172	162	44
17	11	54	89	40
18	5	27	44	43
19	46	144	148	52
20	28	99	106	50
21	139	370	266	49
22	14	46	51	23
23	34	91	99	30
24	73	210	192	69
25	41	124	146	53
26	75	266	235	64
27	27	140	152	49
28	108	288	204	54
29	226	425	355	99
30	65	198	193	59
31	314	787	524	111
32	100	195	222	58
33	192	678	754	135
34	74	294	312	55
35	19	150	180	54
36	87	275	187	53
37	71	269	273	79
38	19	76	87	38
39	58	208	230	66
40	93	347	284	93
41	77	339	298	63
42	40	152	101	39
43	20	123	125	47
44	14	71	64	33
45	8	70	79	26
46	8	63	60	35
47	24	90	122	41
48	15	64	93	29
49	236	634	480	114
50	26	94	79	38
51	306	928	629	136
52	19	68	68	29
53	202	510	351	117
54	24	87	66	35
55	258	667	456	118
56	15	48	46	25
57	23	117	124	56
58	28	97	93	38
59	14	32	165	60
60	51	65	150	43
61	92	105	258	56
62	5	8	45	23
63	52	109	340	112

Table A9.9 Raw data (Pb fractionation) plot I, sub soil.

sample no.	SZn-exc (mg/kg)	SZn-red (mg/kg)	SZn-oxi (mg/kg)	SZn-red (mg/kg)
1	10	6	19	62
2	6	4	8	42
3	6	1	7	29
4	6	1	6	29
5	6	1	6	36
6	5	1	6	35
7	10	3	9	33
8	9	3	9	32
9	10	2	7	33
10	7	3	8	35
11	4	0	4	29
12	5	1	6	34
13	14	3	5	24
14	6	3	6	33
15	5	2	6	29
16	4	2	6	29
17	4	2	9	45
18	13	13	24	81
19	5	2	6	36
20	6	3	8	43
21	6	3	13	38
22	5	2	7	33
23	4	1	5	26
24	4	2	7	36
25	6	3	8	43
26	8	4	7	38
27	6	4	8	41
28	7	3	7	38
29	25	2	4	29
30	5	2	6	32
31	7	3	7	42
32	5	1	6	27
33	5	5	8	32
34	5	6	6	34
35	3	5	8	45
36	4	6	6	39
37	6	5	3	43
38	5	6	6	37
39	5	6	6	39
40	7	6	7	34
41	6	7	6	34
42	5	7	6	36
43	5	7	7	33
44	4	7	7	38
45	5	7	8	45
46	9	5	8	38
47	4	4	7	38
48	4	7	7	56
49	6	3	6	36
50	7	3	6	34
51	4	2	3	36
52	7	3	10	30
53	7	3	3	41
54	7	3	5	38
55	5	2	2	35
56	5	2	5	33
57	7	3	4	46
58	6	3	6	36
59	4	7	6	38
60	6	8	5	33
61	4	7	5	31
62	5	7	6	35
63	7	7	4	44

Table A9.10 Raw data (Zn fractionation) plot I, sub soil.

sample no.	total Pb (mg/kg)	total Zn (mg/kg)	sample no.	total Pb (mg/kg)	total Zn (mg/kg)
1	1496	62	33	1493	60
2	3318	57	34	2232	78
3	547	60	35	469	50
4	422	50	36	563	51
5	3440	46	37	1941	68
6	1825	79	38	684	78
7	3542	51	39	2027	49
8	1242	45	40	294	79
9	4264	65	41	261	63
10	780	40	42	312	61
11	875	35	43	1167	50
12	1720	62	44	2598	65
13	1203	99	45	964	52
14	2918	42	46	304	61
15	218	42	47	1196	68
16	1191	74	48	828	81
17	1563	39	49	1008	46
18	1667	55	50	1416	96
19	2159	41	51	1458	75
20	2830	43	52	1642	39
21	491	47	53	3169	65
22	238	46	54	1048	63
23	735	61	55	1568	52
24	3123	42	56	805	93
25	1004	40	57	1993	114
26	901	67	58	1117	95
27	2491	36	59	523	43
28	242	49	60	698	59
29	446	43	61	1379	51
30	636	50	62	2105	69
31	2788	62	63	1271	61
32	1684	48	64	348	59

Table A9.11 Raw data plot II.

sample no.	total Pb (mg/kg)	total Zn (mg/kg)	sample no.	total Pb (mg/kg)	total Zn (mg/kg)
1	3276	56	62	1877	57
2	2078	48	63	714	91
3	553	34	64	327	69
4	2467	82	65	865	60
5	373	42	66	906	82
6	1633	60	67	2845	81
7	471	84	68	4475	77
8	389	69	69	2229	74
9	1007	58	70	2109	59
10	2387	60	71	1816	42
11	1840	53	72	5164	68
12	3415	72	73	1083	71
13	4375	71	74	603	58
14	216	55	75	588	75
15	161	58	76	342	77
16	305	64	77	744	76
17	2019	100	78	2839	75
18	529	63	79	2527	74
19	373	110	80	8678	79
20	567	70	81	1168	102
21	628	65	82	700	110
22	1484	87	83	2215	80
23	1319	72	84	1048	83
24	3342	53	85	986	78
25	1231	68	86	547	76
26	394	47	87	351	120
27	2231	52	88	1086	76
28	1449	71	89	2078	118
29	848	40	90	994	88
30	325	85	91	1395	114
31	715	70	92	3687	105
32	1261	60	93	1424	82
33	536	63	94	2301	63
34	1011	54	95	1030	101
35	858	57	96	737	90
36	2910	68	97	677	107
37	2167	54	98	394	86
38	1403	63	99	533	75
39	1183	63	100	1659	62
40	781	37	101	1660	73
41	282	50	102	1801	74
42	410	63	103	2789	73
43	670	40	104	2212	98
44	909	41	105	2593	60
45	2203	46	106	709	60
46	4006	53	107	1360	67
47	1624	39	108	435	95
48	917	51	109	251	79
49	3592	62	110	382	79
50	2090	51	111	2956	53
51	1697	81	112	2877	69
52	526	65	113	2417	67
53	409	40	114	2916	44
54	658	48	115	2483	67
55	1288	57	116	392	56
56	2805	56	117	2087	64
57	2355	62	118	1488	80
58	1443	64	119	1171	62
59	1052	70	120	644	68
60	1594	51	121	261	56
61	1980	66			

Table A9.12 Raw data plot III.

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